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THE ABSORPTION OF X-RAYS IN CRYSTALLINE COMPOUNDS

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That the mass absorption coefficient for X-rays in a compound is the sum of the mass absorption coefficients of the component atoms and is independent of the physical state of the absorber, has been proven to be true within the rather large experimental error to which most absorption measurements have been subject. An empirical formula may be used to express the absorption coefficient of compounds and it is the purpose of this note to describe an investigation of the accuracy of this formula during which the author has studied the X-ray absorption of several crystals.

The following empirical formula, given by A. H. Compton,[2] expresses within about 5% the absorption by all elements of atomic number greater than 5 for wave-lengths between 0.08 and 1.4 A.U.:

$$\frac{\mu}{\rho} = \frac{C\lambda^3 N^4 + 0.32N}{A}$$

N is the atomic number and A is the atomic weight of the absorber, λ is the wave-length in A.U. and the best value of C, according to Allen,[3] is 1.36×10^{-2} for wave-lengths shorter than the K critical absorption limit and 1.86×10^{-3} when λ is between the K and L absorption wave-lengths. Upon the assumption that the molecular absorption coefficient is the sum of the atomic absorption coefficients, the above formula becomes, for a compound:

$$\frac{\mu}{\rho} = \frac{C\lambda^3 \Sigma N^4 + 0.32\,\Sigma N}{\Sigma A} \qquad (1)$$

where the summations are taken over each atom in the molecule. Expressions similar to this have been used by several investigators. In case the compound is polar, and one or more electrons may be supposed to have passed from one ion to the other, the question arises whether the N in (1) should be the nuclear charge of the atom, or the actual number of electrons which reside in the ion. For compounds containing moderately

light atoms, the calculated value of the absorption coefficient may vary perhaps 20% as one or the other method of evaluating the N's is adopted.

Consideration of the absorption process shows that the outer electrons are relatively ineffective in absorption. The absorption of an atom depends not so much upon the number of electrons in the atom as upon the distance of the electrons from the nucleus—that is, the energy required to liberate them from the atom. But this energy depends upon the nuclear charge and consequently the N in (1) is the nuclear charge of the atom. In all the attempts at formulating a theory of X-ray absorption,[4] it is shown that the inner electrons are predominant; the lack of periodicity of the absorption coefficient also indicates that the process goes on mainly within the core of the atom. It is to be expected, however, that refined measurements would show a periodicity in absorption coefficient, as well as an effect due to changes of physical or chemical state.

If there is no observable effect upon the absorption coefficient produced by changes in chemical or physical state, the measurements of Wingardh,[5] made largely upon salts in solution, may be used as a basis for calculation of the absorption coefficients of compounds. Wingardh determined the absorption coefficients of a number of elements, as well as those of substances in solution, and prepared a table of atomic absorption coefficients for $\lambda = 0.710$ A.U. In the only instance where comparison between the author's measurements on crystals and those of Wingardh on solutions is possible, the agreement is satisfactory. There seems to be practically no difference between absorption by a compound in solution and in the solid state.

Absorption measurements upon crystalline compounds have been made in very few instances and they have been subject to large experimental error. A peculiar source of error lies in the fact that if the crystal absorber is in such a position that some set of atomic planes is oriented so as to reflect the primary beam, a part of the energy of the primary beam is thereby lost; thus a "selective absorption" is added to the ordinary absorption. W. H. Bragg demonstrated the existence of this selective absorption in diamond.[6] The author, in determining the absorption of a particular slip of rock-salt, found that the coefficient when the crystal was turned so that the primary beam was reflected in the first order by the (100) planes was 11% higher than when the primary beam was parallel to the (100) planes. The amount of this selective absorption—and therefore the change in absorption coefficient—depends upon the reflecting power and perfection of the crystal. For a poor crystal, such as rock-salt, reflection may take place over a rather large range of angles and considerable power will be lost from the primary beam. On the other hand, a good crystal such as calcite reflects only within a very small range of angles, so that, if a primary beam of more than a few minutes' divergence is used,

the relative amount of power lost from it by reflection will not be large. This consideration probably explains why Aurén,[7] using a beam of 2–3° divergence, found selective absorption in rock-salt and sylvine, but not in calcite or gypsum. If the sample under investigation is a powder, which must often be the case, selective absorption will always be present since some of the powder particles will always be in a position to reflect the primary radiation. Consequently, the absorption coefficient of a powder should be greater than that of a single crystal which is not in a position to reflect radiation. As a matter of fact, the amount of radiation reflected by a powder is probably rather a small fraction of the total incident radiation, and the difference in absorption between powder and single crystal is hardly measurable by the ordinary method. Measurements by the author on single crystals of rock-salt and powdered NaCl failed to show a difference in absorption.

A comparison of the measured linear absorption coefficients for $\lambda = 0.710$ A.U. with those calculated by formula (1) for several crystals is given in table 1. Monochromatic Mo Kα radiation was used, and the crystal samples were in the form of a compressed slab of powder. Single crystals of NaCl and CaF_2 were also studied. The thickness of each powder sample was determined from the weight of the slab and the area of its face. Wingardh's values for NaCl and $CaCO_3$ are included in the table.

TABLE 1

CRYSTAL	DENSITY (ρ)	μ (OBS.)	μ (CALC.)	μ (WINGARDH)
NaCl	2.161	17.5	18.0	18.1
LiF	2.62	4.6	3.7	..
NaF	2.79	7.2	7.3	..
CaF_2	3.18	36.2	35.0	..
$CaCO_3$	2.71	..	23.3	23.4

It appears from the table that the absorption coefficients of all the crystals except LiF are represented with considerable accuracy by formula (1). The LiF had been carefully purified and contained almost no impurity; but formula (1) could hardly be expected to apply in the case of LiF, as the atomic absorption of Li, whose atomic number is 3, is probably not represented accurately by the atomic absorption formula.

[1] NATIONAL RESEARCH FELLOW.

[2] A. H. Compton, *Bull. Nat. Research Council*, No. **4**, 1920.

[3] Allen, *Physic. Rev.*, **27**, 266, 1926.

[4] A. H. Compton, *Ibid.*, **14**, 249, 1919. L. de Broglie, *J. Physique*, **3**, 33, 1922. Kramers, *Phil. Mag.*, **46**, 836, 1923.

[5] Wingardh, *Zeit. Physik*, **8**, 365, 1921.

[6] W. H. Bragg, *Phil. Mag.*, **27**, 881, 1914.

[7] Aurén, *K. Vet. Akad. Nobelinst. Stockholm Meddel.*, **4**, Nos. 3, 5, 10, 1921.

ACOUSTIC PRESSURES IN CASE OF SOAP BUBBLES[1]

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The acoustic pressures encountered in the present[2] experiments are often many times larger than the pressures within a moderately sized soap bubble. One might infer therefore, that such a bubble could actually be blown with the telephonic apparatus and pinhole probe described. It seemed worth while to try this with an apparatus sketched in figure 1, where TT' are the two telephones vibrating in series and tt' the acoustic pipe joining them. At s is the salient pinhole. The quill tube rU connects with the interferometer U-gauge for registering the acoustic pressure, s. A T-branch at f carries a small funnel, from which the bubble B may be blown. A second T-branch at e with a stopcock may be used for blowing the bubble; but it is usually more convenient first to blow the bubble from f and insert it. If desirable a second pinhole may be used at r, in series with s.

If the bulb B is rigid, even a flask of half a litre capacity, the acoustic pressure at U appears at once and in these experiments was about $s = 250$. With an appreciable leak in the flask it fell immediately to zero. Hence the apparatus itself was in good condition.

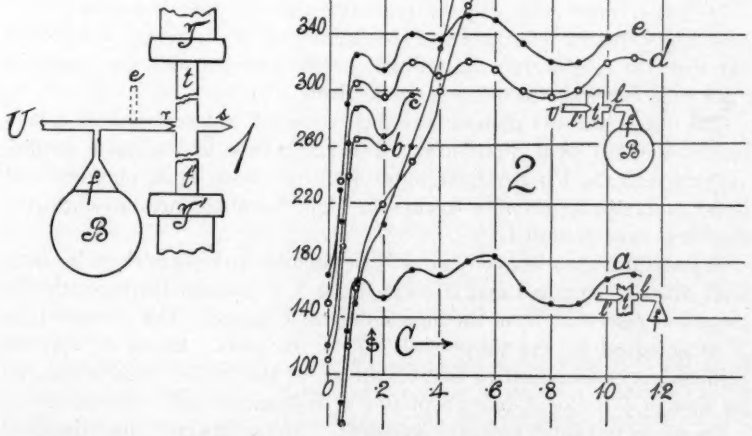
Soap bubbles of various sizes were now blown and attached as shown. In every case the pressure fell to the value corresponding to the radius of the bubble. With large bubbles, $s = 60$, with smaller ones $s = 50$, for instance, were recorded all much within the acoustic pressure inside a rigid system. This pressure decreased about 10% when the telephones were silenced and increased again when they sounded—a result to be expected since the air of the bubble escapes slowly at the pinhole s, in the absence of acoustic vibration. For the same reason, s slowly increases as the bubble contracts. While the telephones are sounding moreover, there is no escape of air from the pinhole and the pressure s remains constant till the bubble bursts, some time after.

Thus to develop the acoustic pressure in full requires rigid walls throughout. One might have supposed that in the endeavor to reach the limit of this pressure there would be current at s figure 1; i.e., continual inflow of air in the direction sr, in which case, the bubble would be inflated with continually decreasing interval pressure; but this is not the case and the acoustic pressure cannot rise above the resistance corresponding to the elastic walls. Current at s inward is impossible, though any outward flow is checked when acoustic vibration occurs.

2. The inversion of this experiment is of particular interest. The

adjustment is sketched in the insert, figure 2, curve *d*. The bubble *B* with its funnel *f*, here replaces the outer quill tube *l* and thus the bubble contributes an increment to the atmospheric pressure in *tt'*, the pipe joining the telephones. The pinhole probe *l'* communicates with the U-gauge, as usual, with a quill 17 cm. long.

In the absence of the bubble, the low graph, figure 2, *a* was obtained. The small acoustic pressures here are the result of the necessarily long quill tube connector *l* (12 cm. long) in this experiment; for with the 2 cm. quill the graph takes the high excursion shown at *h* in figure 2. It does not differ much from the graph *g*, obtained in the former experiment, when the funnel *f* depending from *l'* is closed by a plug of liquid.



Bubbles were now blown of different sizes and attached at *l*. Examples of the results are recorded by the graphs *b*, *c*, *d*, *e*, in the first two of which the bubble burst early. Curves *d* and *e* however, were carried through much further without mishap. It will be seen that these graphs are exactly like graph *a* in shape, throughout; but they are all raised to different high *s* values owing to the surface tension of the bubble *B* (see insert) attached to the funnel *f*.

Thus the pinhole probe *l* builds up the acoustic pressure in the gauge *U*, from whatever pressure it finds in the sounding pipe *t*, provided the *Ul'*

system is rigid. If it is not rigid, the limiting pressure of the elastic walls cannot be exceeded. The graph h rises so rapidly that the crests in $ab \ldots e$ are present, if at all, as mere sinuosities; but four of these may be recognized, all displaced toward lower pitch (larger C values) as compared with the $a \ldots e$ graphs.

[1] Advance note from a report to the Carnegie Inst., of Washington, D. C.

[2] The telephones were actuated in series by an electric oscillating circuit whose pitch is controlled by the capacity, C. The corresponding fringe displacement, s, measures the acoustic pressure. These PROCEEDINGS, **12**, p. 137.

ACOUSTIC PRESSURE PROMOTED BY COÖPERATING QUILL TUBES WITHOUT PINHOLES[1]

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1. *Long, inner quill.*—In the preceding papers,[2] pinhole probes of successively different lengths either counteracting or in series, were tried out with the results that the acoustic pressure varied with the length of quill tube carrying the pinhole, periodically.

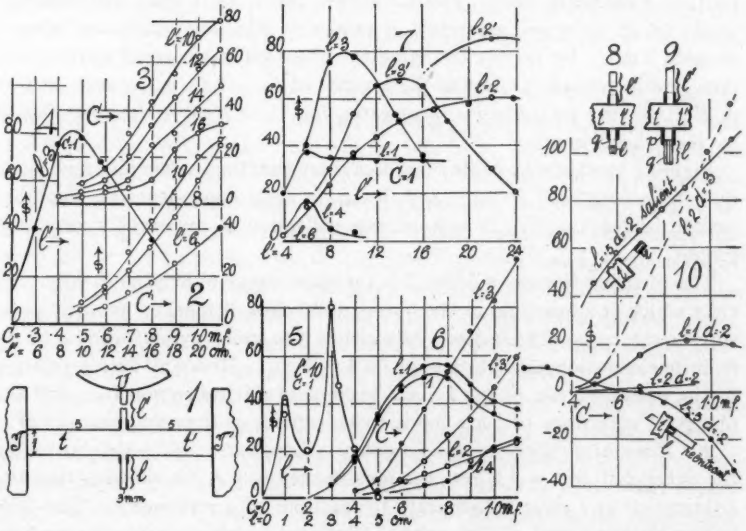
The outer (salient) pinhole was then removed and replaced by a succession of clear bore quill tubes. Periodic results of the same nature, varying with the length of the outer quill tube were again obtained and under favorable length adjustments the highest acoustic pressures hitherto detected were recorded.

It is natural therefore to remove both pinholes, to replace them by clear quill tubes of lengths l and l', as in figure 1, l' communicating with the capacious reservoir, U, of the interferometer U-gauge. The acoustic pipe tt' is actuated by the telephones T,T' at its ends. Hence tt' may be regarded as communicating freely with air, at the further ends of l and l'; for though U is closed, it is about 10 cm. in diameter and 1 cm. deep.

Owing to the small acoustic pressures, s, to be expected, the fringes of the interferometer were enlarged. The pitch of the oscillating circuit actuating T,T' was varied by changing its capacity, C.

In the experiments given in figures 5 and 6, the inner quill was left constant at $l' = 10$ cm., while the outer was varied in succession from $l = 0$ to $l = 7$ cm. No fringe displacements s were obtained at $l = 0$ ($^1/_4$ inch tubulure in tt'), nor above $l = 5$ cm. of quill tube length. The curve ($l' = 10$) on the left, records two sharp cusps at $l = 1$ and 3 cm., a curious result to be interpreted by the aid of the curves, figure 6, on the right, in which C is varied from 0.4 to 1.1 microfarad for each value of l.

The C-graphs for $l = 1$ cm. are different in type from the others ($l = 2, 3, 4$ cm.), showing a well developed crest at $C = 0.75$ microfarad. They change in value with slight differences of adjustment of the short quill tube, $l = 1$ cm., so that two graphs are given as examples. On the other hand, from $l = 2$ cm., which is again low in s, the graphs rise with great rapidity to the graph for $l = 3$ cm. Again two curves, $l = 3$ and $l = 3'$, are given, the change being due to slight alterations in the insertion of the 3 cm. quill tube. From the high values of acoustic pressure s for $l = 3$, the graphs fall again to the low values for $l = 4$ cm. and to zero at $l = 5$ cm. This curious kind of variation, as exhibited in the graph, figure 5, $l' = 10$ cm., may be referable to two independent crests superposed.



The acoustic pressures s are always positive, showing that the l' quill is dominant; but for $l = 0$ and l above 5 cm. all acoustic pressure vanishes. The very steep cusps of the s, l graph indicate the great delicacy of vibrational equilibrium. It is difficult to reinsert the outer quill so as to quite reproduce an original graph.

In figures 2, 3 and 4 the conditions are reversed; the outer quill is kept constant at $l = 3$ cm. (favorable length in figure 5), while the inner quill is extended from $l = 0$ to $l = 16$, in steps of 2 cm. In the C-graphs figures 2 and 3, there is an accelerated rise of acoustic pressure, s, below $l' = 6$ cm. A maximum of s-values is reached at about $l' = 10$ cm. Thereafter the s-values gradually fall again with changes in the form of the C-graphs. The variations as a whole are exhibited in the s, l' graph, figure 4.

The present phenomena are therefore more uniform in character than the preceding, figure 5. For $l = 0$, or 5, 7, to 20 cm., no acoustic pressures ($s = 0$) were obtainable. On either side of about $l = 3$ cm. the graphs therefore fall off abruptly, as heretofore.

Thus the acoustic pressures must be regarded as produced by the nodes of the inner quill l', figure 1; but this is ineffective, except in the presence of short critical lengths of the outer quill, l. Since both quill tubes are clear, such a difference of behavior is only referable to the fact that l' terminates in the closed though capacious U-tube reservoir, whereas l is open to the atmosphere.

A systematic repetition of the work, given in part in figure 7, added nothing essentially new. The Cs curves for ($l = 1$ cm.) all exhibited crests at an intermediate pitch, a tendency which is quite lost when l exceeds 2 cm. By merely changing the insertion of the outer quill, $l = 2$ cm., it was possible to double the s value at $C = 1$ m. f., as seen at $l = 2, 2', 3, 3'$ cm.; by adding a short extension, the Cs curve dropped almost to zero throughout.

Figure 7 gives the acoustic pressures corresponding to the different outer quill tube lengths, $l = 1, 2, 3, 4, 6$ cm. in their dependence on the inner quill tube lengths, l'. It is a curious collection of apparently unrelated graphs.

The puzzling feature of figure 7 is the short range of lengths ($l = 1 \ldots .4$ cm.) which is admissible in the outer quill tubes, if marked acoustic pressures s are to be obtainable. Meanwhile the inner quill l' admits of indefinite elongation, except perhaps for $l = 1$ cm. Hence all details relative to the insertion, etc. of the l quills become of critical importance and the observed variations of s are liable to be capricious over wide ranges of s.

2. *Reversal of the preceding adjustment. Long outer quill.*—On shortening the outer quill to $l = 1.8$ cm., the pressure fell to $s = 60$, showing that the adjustment at l must be accurate to fractions of a millimeter. The bore is equally important, as if a critical frictional resistance were in question.

The desirability of inverting the character of the preceding experiments, by using the shortest possible l' pipe (junction of the tt' pipe with the U-gauge reservoir) and elongating the l quills, thus presented itself. Would the results in s be symmetrical and acoustic dilatations result from such a reversal? This was pronouncedly not the case. Even when a bulb similar to a Helmholtz resonator was added at l, to balance U at l', there was no noteworthy result.

3. *Quill tubes of constant external diameter, reduced in length and bore conjointly.*—We finally come to a probable solution of the preceding intricacies. Quill tubes, inserted coaxially with short pieces of rubber tubing are necessarily shouldered at one end. The tube q, figure 9, thus effects a reduction of the diameter of the anterior tubulure p and may therefore

in a measure take the place of a pinhole. To test this surmise, tubes of the same diameter but of small bore, the length of which is successively diminished, may be taken. The adjustment is shown at in figure 8 where l is the length of small bore tube inserted in the wider quill q. As before tt' is the telephone pipe with the quill tube l' (here 27 cm. long for convenience), joining tt' with the U-gauge. In figure 10 the Cs graph for the former quill tube (l = 2 cm., diameter d = 0.3 cm.) is repeated from the preceding experiments, for comparison.

The other graphs of figure 10 refer to the small bore tubes d = 0.2 cm. in diameter and respectively l = 2, 1, 0.5 cm. in length in question. In the former case they are inserted saliently; in the latter (l = 0.5 cm., see inserts), the insertion may easily be made at the rear (reëntrant) or at the front end (salient) of a short piece of slender rubber tubing (2 cm. long, 0.5 cm. diameter), acting as a quill stem.

When l = 2 cm. the graph is more often slightly negative than positive as in figure 10. When l = 1 cm. the saliency of the insertion is manifested as s is positive within the limits of C; but by a different insertion of l, this graph could have been made negative. When l = 0.5 cm. we have an approach to a coarse pinhole. Placed in the outer end of the rubber junction with tt the corresponding graph is strongly positive. Placed at the inner end of the junction with tt', the graph soon becomes strongly negative, though it is a complicated graph with double inflections. At all events the short capillary tube with rubber prolongation now acts like a pinhole probe with a node on the inside of the rubber quill, at the constricting hole. The Cs graphs change sign on reversal.

It is now clear that if the work of figure 10 were continued, by further reducing both l and d of the constriction conjointly, the relatively enormous full pinhole effect in s would ultimately be reached, without any need of slope in the walls of the pinhole. Whether this is conical or not seems to be without consequence. A node at the pinhole inside the quill tube, the latter functioning like a closed organ pipe, is thus accountable for the acoustic pressure s; and s increases with the intensity of the node, i.e., with the increased perfection in the tuning of the probe relatively to the acoustic pipes, like tt'. The node carries the excess mean pressure over atmospheric pressure. The stream lines run from the pinhole into the quill tube of the probe, regarded as a closed organ pipe. Hence if the pinhole node is within the acoustically vibrating region tt' (organ pipe with salient pinhole probe) there is acoustic pressure; if the pinhole node is outside of the region tt' (reëntrant pinhole probe) there is mean dilation in tt'. A single pinhole may be reënforced by a second one in series with it, between tt' and the U-gauge.

The reversed experiment was equally decisive. The inner quill l' (cf. figure 1) was kept 15 cm. in length and this carried the cylindrical

constriction l'' (0.5 cm. long, $d = 2$ mm.), immediately adjoining tt'. The outer quill was elongated from $l = 2$ cm. to $l = 16$ cm.

As it takes some time to work out any one of the *Cs* graphs, the *ls* graph was investigated directly for $C = 1.0$ microfarad and $l = 15$ cm. The strong cusplike maximum for $l = 2$ cm. was here again encountered and its sharpness showed the accuracy of tuning the l length, required. Beyond this range of lengths (above $l = 16$ cm.) there was to be another, but flat crest.

Thus we have here again the pinhole effect on a small scale, which could be increased by simultaneously decreasing l'' and d of the cylindrical constriction simulating the pinhole to a critical value.

[1] Advance note from a report to the Carnegie Institution of Washington, D. C.

[2] These PROCEEDINGS, **11**, 1925, p. 728; *ibid.*, **12**, 1926, pp. 137, 223.

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*NOTE ON THE TEMPERATURE RELATIONS OF PHOTO-ELECTRIC EMISSION AND THERMIONIC EMISSION OF ELECTRONS**

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According to my theories, as expressed in papers printed some years ago,[1] the increase of total potential of "associated electrons" with rise of temperature of the metal is given by the expression $d(P + Pa)/dT$. In the region from 0°C. to 100°C., the only temperature region I have undertaken to deal with, the value of this quantity, expressed in volts per degree, is about -0.000026 for iron and about -0.000065 for bismuth, values for other pure metals studied lying between these limits. The negative sign here indicates, according to my convention, that the work done against attractive or repulsive forces in detaching an associated electron from an atom and taking it completely out of and beyond the influence of the metal increases with rise of temperature; but the indicated rate of this increase is very small. The actual work of photoelectric emission, measured in potential change, being about 5 volts, the indicated change per degree is in general only about one 10^{-6} part of this. If we assume that the kinetic energy of an associated electron is not a function of temperature, this showing is in excellent accord with the observed fact that the greatest wave-length, the lowest frequency, effective in producing photo-electric emission is very nearly independent of the temperature of the metal.

* This note is a development of the concluding paragraph in a paper by the author in the *Physical Review* for August, 1926.

But according to my theorizing the energy required to change an electron from the "associated" state to the "free" state *within* a metal is

$$\lambda' = \lambda'_c + sRT, \tag{1}$$

where λ'_c and s are constants, and the rate of increase of this quantity with rise of temperature is $s\,R$ ergs per degree. If we take 2.5 R as the gas energy, kinetic and potential, per degree per free electron both inside and outside the metal, we have $(s-2.5)R$ left as the increase per degree in the work done against attractive or repulsive forces in changing an electron from the associated to the free state within the metal. Accordingly, since the total work done against resisting forces in the passage of an electron from the associated state within a metal to the free state outside the metal is practically independent of temperature, the work done against such forces in removing an electron from the "free"state within a metal to the free state outside the metal should be found to diminish with rise of temperature at the rate of $(s-2.5)$ R ergs per degree. That is, the quantity just defined can, within the region of temperature considered, be expressed as

$$c-(s-2.5)RT \text{ ergs}, \tag{2}$$

where c is constant.

Now this proposition will doubtless seem at first to be in conflict with Richardson's emission equation in either of its forms,

$$i = AT^{1/2}\epsilon^{-b_0/T}, \tag{3}$$

or

$$i = CT^2\epsilon^{-d_0/T}. \tag{4}$$

For b_0 in equation (3), and d_0 in equation (4), is usually, I think, understood to be $1/R$ times the work of overcoming the resisting forces during the thermionic emission of an electron; and each of these quantities is taken to be a constant.

It must be remembered, however, that neither of these equations can strictly be regarded as standing on a firm logical basis. Richardson assumes the numerator in the exponent of ϵ to be independent of temperature and then shows that, with this assumption, either form of the emission equation corresponds very well with the experimental data. But evidently, a being any constant, we can write (3) as

$$i = AT^{1/2}\epsilon^{-a}\epsilon^{aT/T}\epsilon^{-b_0/T} = A'T^{1/2}\epsilon^{-(b_0-aT)/T} \tag{5}$$

where, in the third member, A' is a constant, while the numerator of the exponent of ϵ has become a variable, subject to a constant rate of change with change of T. Yet this third member of (5) is, so far as the test of experimentation goes, the exact equivalent of the second member. We can of course make a like transformation of equation (4).

There is, apparently, neither theoretical nor experimental proof that the work done against resisting forces in the thermionic emission of an electron is independent of temperature. It may, so far as we know, be of the form (2) given above, as indicated by the theory of dual conduction, and in this case the a of (5) is $(s-2.5)$, a quantity which varies from metal to metal and in iron may, according to my calculations, be as large as 12.5.

[1] See *Proc. Nat. Acad. Sci.*, **7**, p. 105.

THE DIELECTRIC CONSTANT OF DIATOMIC DIPOLE-GASES ON THE NEW QUANTUM MECHANICS

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A treatment of the dielectric constant of diatomic dipole-gases based on the classical quantum theory of multiply periodic systems has been given by Pauli.[1] An attempt has later been made by Pauling[2] to introduce half-quantum numbers into the theory in a rather artificial way. The problem is, however, amenable to the methods of Heisenberg's quantum mechanics,[3] and a complete solution can be given, since frequencies and amplitudes in the case of a rotator capable of orientation in space are now known.

The mechanical system, the quantum analogue of which we are considering, consists of two point masses, m_1 and m_2, capable of rotating about their common center of gravity. We may assume them to be rigidly connected together, since, as will appear later, in the cases to which the theory is applied the distance of separation is only inappreciably changed by the rotation. The system will then be characterized by this distance, a, and furthermore by an electric moment μ parallel to the line joining the masses. To remove degeneration, we imagine a constant magnetic field applied so that the motion consists of a rotation about an axis through the center of gravity and a precession of this axis about the direction of the field, the moment of inertia about such an axis being

$$I = \frac{m_1 m_2}{m_1 + m_2} a^2.$$

The stationary states of the corresponding system in the quantum theory are characterized by two quantum indices j and m, which are related to the terms M^2 and M_z of the diagonal matrices representing the square of

the total moment of momentum and its component in the direction of the magnetic field by

$$M^2 = \left(\frac{h}{2\pi}\right)^2 j(j+1),\ M_z = \frac{h}{2\pi} m.$$

(See, e.g., the recent article by L. Mensing[4] in which the more general system of a diatomic molecule with variable distance between the nuclei is discussed in connection with the oscillation-rotation spectra). For the system under consideration j has integer values starting with $j = 0$ and for a given value of j, m may have any integer value from $-j$ to $+j$ inclusive. If the magnetic field removing the degeneration is small, the energy differences between the various states with the same j and different m will be inappreciable compared to those between states with different j and the energy for all of them will be given by[3]

$$W_j = \frac{h^2}{8\pi^2 I}(j^2 + j + 1). \tag{1}$$

(In Heisenberg's paper one finds $(j^2 + j + {}^1/_2)$, the reason being that Heisenberg forgot to take into account the fact that the rotator with a fixed axis can rotate both clockwise and counter-clockwise. By taking the rotator in space this difficulty is avoided and the above result obtained.) It has been shown[5] that only the amplitudes corresponding to changes of j by unity and of m by 0, ± 1 are different from zero. According to the frequency condition the corresponding frequencies (neglecting again energy differences due to different orientation in the external field) are given by

$$\nu(j, j-1) = -\nu(j-1, j) = \frac{h}{4\pi^2 I} j. \tag{2}$$

The vector matrix representing the electric moment of the system has as components:[4]

$$P_x^0(j, m; j-1, m-1) = -\frac{i\mu}{2}\sqrt{\frac{(j+m)(j+m-1)}{(2j-1)(2j+1)}}, \tag{3}$$

$$P_x^0(j, m; j-1, m+1) = \frac{i\mu}{2}\sqrt{\frac{(j-m)(j-m-1)}{(2j-1)(2j+1)}}, \tag{4}$$

$$P_z^0(j, m; j-1, m) = \mu\sqrt{\frac{j^2-m^2}{(2j-1)(2j+1)}}, \tag{5}$$

if the magnetic field is in the direction of the Z-axis.

The problem now is to find the components independent of the time, i.e., the diagonal components, in the matrix $\mathbf{P}_z$ when a constant electric field E is applied parallel to z. The perturbation theory which, as shown by

Born, Heisenberg, and Jordan,[5] gives the same result as Kramers' dispersion formula[6] when applied to the case of a constant field leads to

$$P_z^1(j, m;\ j, m) = -\frac{2E}{h}\sum_{j', m'}\frac{P_z^0(j, m;\ j', m')\ P_z^0(j', m';\ j, m)}{\nu(j, m;\ j', m')}.$$

Making use of (2) and (5) we easily find:

$$P_z^1(j, m;\ j, m) =$$

$$\frac{8\pi^2 IE\mu^2}{h^2}\left[\frac{(j+1)^2 - m^2}{(j+1)\ (2j+1)\ (2j+3)} - \frac{j^2 - m^2}{j(2j-1)\ (2j+1)}\right] =$$

$$\frac{8\pi^2 IE\mu^2}{h^2}\ \frac{3m^2 - j^2 - j}{j(j+1)\ (2j-1)\ (2j+3)}. \qquad (6)$$

In the limit of large quantum numbers this goes over into the classical expression

$$P_z^1(j, m;\ j, m) = \frac{4\pi^2 IE\mu^2}{h^2 j^2}\left(\frac{3m^2}{2j^2} - \frac{1}{2}\right).$$

(See, e.g., Pauli.[1])

The probability of an atom being in the state j, m is given by

$$\frac{e^{-W_j/kT}}{\sum_{j, m} e^{-W_j/kT}},$$

the summation extending over all states, if again we neglect the energy differences of the states having the same j but different m. The dielectric constant ϵ due to the permanent moments of the molecules is then given by

$$\frac{3}{4\pi}\frac{\epsilon - 1}{\epsilon + 2} = \frac{N\sum_{j, m} P_z^1(j, m;\ j, m)e^{-W_j/kT}}{E\sum_{j, m} e^{-W_j/kT}},$$

where N is the number of molecules per cm.[3] Substituting the value for P_z^1 from (6) and performing the summation over m in the numerator we find it to give zero for all values of j except $j = 0$, since

$$\sum_{-j}^{j}{}_m\ (3m^2 - j^2 - j) = 0.$$

For $j = 0$ (and hence $m = 0$), however, we get

$$P_z^1 = \frac{8\pi^2 IE\mu^2}{3h^2} \qquad (6a)$$

and hence

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=\frac{8\pi^2NI\mu^2}{3h^2}\frac{1}{\sum_{j,m}e^{-(W_j-W_0)/kT}}. \tag{7}$$

This vanishing of the sum for all values of j except $j = 0$ is quite analogous to what happens in the classical theory. There the molecules in that region of the phase space for which the energy is greater than $2\mu E$ (the zero of the energy scale being so chosen that the molecules completely at rest have an energy 0) do not contribute at all to the polarization (see, e.g., Alexandrow[7] or Pauli[1]). In the classical theory this theorem is rigorously true while we have only proved its quantum analogue to terms proportional with E, although it is probable that it really is rigorous here too. There is, however, this difference that in the classical theory perturbation considerations cannot be applied to all the molecules which contribute, the energy due to the electric field being comparable to that of rotation for some of them, while in the quantum mechanics this difficulty disappears due to the zero-point energy of the lowest state. In confirmation of the result that this state has an induced moment proportional to E measurements by Barker[8] show the absence of a linear Stark-effect in the oscillation-rotation spectra of HCl even for the lowest state, a fact pointed out already by Mensing.[4] It should further be remarked here that if the electric field be chosen in the X-direction, i.e., at right angles to the magnetic field, it is found, by the aid of (3) and (4), that just as before only the molecules in the lowest state contribute to the polarization, the moment in the X-direction being given by (6a). The space quantization hence does not make the diatomic gas anisotropic as regards the dielectric constant, a possibility which had been suggested by Ruark and Breit.[9] This case is thus similar to that of a monatomic gas where the same remark applies.

We next wish to evaluate the sum in the denominator of (7). Remembering that to every value of j there correspond $2j + 1$ values m and substituting the values W_j from (1) we get for this sum

$$S=\sum_0^\infty{}_j\,(2j+1)e^{-\alpha j(j+1)},$$

where

$$\alpha=\frac{h^2}{8\pi^2IkT}. \tag{8}$$

Later we shall see that in the cases where data are available α is small (about 0.05) and hence the series very slowly convergent. The series can, however, in first approximation be put equal to the integral

$$S_0=\int_0^\infty(2x+1)e^{-\alpha x(x+1)}\,dx=\frac{1}{\alpha}.$$

As a second approximation we consider rectangles erected over the X-axis with the bases extending from j to $j+1$ and their heights equal to $(2j+1)e^{-\alpha j(j+1)}$. The difference between S and S_0 is the sum of the triangular pieces with one curved side between the rectangles and the curve of the integrand. The area of these pieces we compute by Simpson's rule, and it is easily found to be equal to $S_1 = 1/3$. Adding it to S_0 we find

$$S \sim S_0 + S_1 = \frac{1}{\alpha} + \frac{1}{3} \sim \frac{1}{\alpha(1-\alpha/3)}.$$

Hence putting for α its value (8)

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2} = \frac{N\mu^2}{3kT}\left(1 - \frac{h^2}{24\pi^2 IkT}\right). \tag{9}$$

It is interesting to note that for temperatures large enough to make the second term negligible, this is identical with Debye's expression derived on the classical theory even as regards the numerical factor.

Zahn[10] has made measurements of the dielectric constant of the hydrogen halides and its dependence on temperature. These molecules have no electronic moment of momentum, and hence (9) applies if a term independent of T is added to take care of the electronic displacements inside the molecules, so that

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2} = \frac{N\mu^2}{3kT}\left(1 - \frac{h^2}{24\pi^2 IkT}\right) + N\beta,$$

β being the polarizability per molecule. Here the second term in the parenthesis $\theta/3T$ is very small in the temperature region investigated, θ having a value around 10 for these gases, as determined from measurements on band spectra by Kratzer[11] and Czerny,[12] while T ranges around 300°. The term under consideration is hence about 0.01, which is near the limit of precision attained by Zahn. The values of μ are, therefore, the same as those found by Zahn, since he used Debye's expression. With his values of μ it is easily seen that in electric fields of ordinary strength, the additional energy due to the field and the energy differences between molecules having the same j but different m are indeed very small compared to those between molecules with different j, as assumed in the statistical calculation. For this reason Barker[8] could not notice even a quadratic Stark effect in the HCl bands. Furthermore the assumption of rigidity is well justified.

It is also seen from Zahn's results that the moment induced in the molecule due to electronic displacements for the lowest state is small compared to that obtained in (6a) in a ratio of about 1:100 and that the latter is at least five times as large as the moment computed from (6) for any of the molecules in the other states. If the Stern-Gerlach experiment be

performed on these molecules with an inhomogeneous electric instead of a magnetic field, the molecules would suffer a displacement

$$s = \frac{Pl^2}{6kT} \frac{\partial E}{\partial z}, \tag{10}$$

(see Stern[13]) if they travel through a distance l in a field at right angles to their velocity with an inhomogeneity $\partial E/\partial z$, and if they have an average velocity corresponding to a thermal agitation at the temperature T. By shooting the molecules parallel to a charged wire in vacuum we can easily make E about 2.10^5 volt/cm. $\partial E/\partial z$ about 10^6 volt/cm., $l = 5$ cm., $T = 300°$. For the state $j = 0$ we get with the help of (10), for s a few tenths of a mm., which is easily measurable. The remaining molecules would suffer deflections less than 1/5 of this.

The transition probabilities of absorption in the pure rotation spectrum of the molecules are given by

$$b\,(j, j+1) = \frac{8\pi^3 \mu^2}{3h^2} \cdot \frac{j+1}{2j+1}.$$

The right-hand side is known if μ is known, while the left-hand side may be computed from the absolute value of the absorption in the pure rotation spectrum. Such calculations have been made by Tolman and Badger[14] from Czerny's[12] measurements for HCl. The value of the left-hand side is, however, only about 1:20 of that of the right-hand side with Zahn's[10] value of μ. This is probably due to the fact that the resolution of Czerny's grating was inadequate. That poor resolution may falsify measurements of the absorption coefficient by a factor of 10 is pointed out in a recent paper by Minkowski.[15]

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A PHOTO-IONIZATION EXPERIMENT WITH HYDROGEN

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A sensitive method of detecting photo-electric ionization of a gas has been described by Dr. Foote and the author.[1] The gas is contained in a two-electrode, thermionic tube with conditions so adjusted that the electron current is limited by space charge. Production of positive ions by incident radiation will neutralize the space charge and produce a very much magnified change in the thermionic current. A paper now in press[2] describes measurements of the photo-ionization of some monatomic gases by a discharge in the same gas. A double thermionic tube was used in which one unit produced a discharge at controlled current and voltage while the other unit detected photo-ionization excited by the radiation from the discharge. Electrical shielding prevented diffusion of ions and electrons from one thermionic unit to the other. The experiments showed that little if any photo-ionization is produced with discharge voltages equal to or less than the first ionization potential but that there was a large effect at potentials sufficient to give double ionization or soft X-ray excitation. Thus the effect furnishes a sensitive method of detecting any critical potentials which give rise to radiation of higher frequency than the first absorption limit of the normal atom, and the principle should be equally applicable to polyatomic molecules.

Recently experiments have been carried out with hydrogen to see if there is any photo-ionization of this gas by its own radiation. The tube was similar to the one used before[2] and a preliminary test with argon showed that high sensitivity could be attained. Hydrogen was streamed continuously from an electrolytic generator through hot platinized asbestos, a capillary tube, a liquid air trap, the discharge tube, and a second liquid air trap. The pressure was generally 0.02 mm. but higher pressures were tried with no significant change in the results.

In general there was an easily measurable photo-ionization beginning near 13 volts, increasing abruptly at 16 volts and gradually approaching saturation at higher voltage. This effect, however, was not of constant magnitude and was traced to the falling of the level of the liquid air around the traps. It was probably caused by ionization of a trace of water vapor by the hydrogen radiation. After raising the level of the liquid air the photo-ionization would gradually drop to as low as one per cent of the initial value. The small residual effect changed with the discharge voltage in the same manner as before and can safely be ascribed to the same cause. In one instance this minimum change in

electron current produced by radiation was 6×10^{-8} amps. at 40 volts or 1.5×10^{-4} times the discharge current while in argon under comparable conditions the photoeffect was about one-twentieth of the discharge current.

I conclude that there is no evidence that hydrogen emits radiation which is capable of ionizing the normal molecule. Spectroscopic results seem to be consistent with this conclusion for no hydrogen lines have been identified beyond 885 Å corresponding to 15 volts.[3] My negative results are of significance because the method seems to be particularly adapted for the sensitive detection of such radiation.

This conclusion has some bearing on the important theoretical problem of the structure of the hydrogen molecule ion. It requires about 15.9 volts to produce H_2^+ by electron collision[4] and presumably a quantum of radiation of equal or greater energy than this can produce photoionization. We would not expect either H_2 or H to be capable of emitting such radiation but there remains the possibility that H_2^+ may have excited states of greater energy than 15.9 volts which could give rise to ionizing radiation. Production of such states would require a double excitation which could be effected either by successive electron collisions at some voltage greater than 15.9 or by a single electron collision at a voltage greater than 31.8 volts. Under the experimental conditions the excitation by single collision would be most probable and the range from 30 to 50 volts was carefully covered in the observations. The negative results indicate that the excitation potentials and presumably the ionization potential of H_2^+ are less than 15.9 volts.

Witmer[5] has recently given spectroscopic evidence that the minimum energy required to produce H_2^+ is 15.2 volts and he has suggested that ionization by electron collision necessarily gives vibrational energy to the ion so that the critical potential does not measure the work required to produce a normal ion. This consideration merely lowers a little the above estimates of the excitation potentials for ionizing radiation.

The model first proposed by Bohr[6] for H_2^+ has an ionization potential of 11.9 volts. He has pointed out that the model is dynamically unstable and Pauli[7] and Niessen[8] have shown that there is a stable model with an ionization potential of 7.00 volts. These models are consistent with our results in that the ions cannot give out ionizing radiation.

On the other hand Langmuir[9] and Urey[10] have shown that a model in which the electron performs linear vibrations perpendicular to the line joining the nuclei has an ionization potential of 16.65 volts. All excited states of total quantum number 4 or more could give rise to ionizing radiation if we accept Witmer's value for the ionization potential of the molecule. My conversations with Dr. Urey relative to the linear model suggested the present research.

* Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

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SERIES AND IONIZATION POTENTIALS IN THE IRON SPECTRUM

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The iron spectrum has been extensively investigated especially by F. M. Walters[2] and by the writer.[3] A brief discussion of the iron energy diagram as given in these papers from the viewpoint of the theory of spectra with several valence electrons[4] was first given by F. Hund.[5]

It is the object of the following lines to discuss again the iron spectrum theoretically in a more detailed fashion than has been possible before, to show how far the theory enables us to predict not only the existence, but also the position of unknown terms, and finally to use these predictions for the establishment of several short series. We shall furthermore have the opportunity to demonstrate with a special group of terms the action of Pauli's equivalence principle.[6] Anticipating the result, we may say that not only is the theory in complete agreement with empirical facts even in minute details, but also that it serves as an efficient tool for detecting new regularities.

Figure 1 shows the energy diagram of the iron spectrum in its present state. Compared with the other energy diagrams of Fe as published by W. F. Meggers[7] or W. Grotrian[8] several terms have been added, one of which was found by Dr. F. M. Walters and kindly put at the writer's disposal (^3P at 23,000 cm.$^{-1}$), whereas others which are of importance here will be described and discussed later.

In explanation of figure 1, it may be said that the terms of equal apparent azimuthal quantum l are drawn on vertical lines. Each term is repre-

sented by a rectangle, whose vertical height corresponds to its separation in sublevels. Terms of different series systems are distinguished by their position on the vertical line, so that quintet terms (middle system) are drawn on the line, whereas triplet and septet terms are on the left and right sides of the line, respectively.

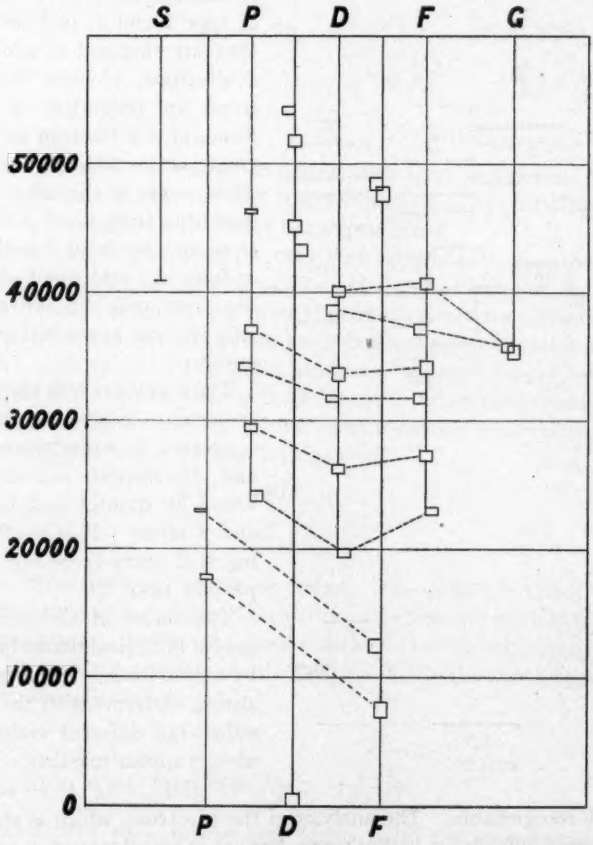


FIGURE 1

Primed and unprimed terms are put on different vertical lines and we have consequently two adjacent vertical lines for each l value. In terms of the old "dash" notation[9] the arrangement of the terms from left to right is the following: $\overline{S}, \overline{P}, P, D, \overline{D}, \overline{F}, F$..... A glance at the niveau scheme shows that $\overline{P}$, D, $\overline{F}$, etc., terms are low; $\overline{S}\ P\ \overline{D}\ F$...terms are high; so that, as was proposed by Russell[10] two sets of terms should be dis-

tinguished according to their position. In our arrangement the second, fourth and sixth vertical lines bear the low set, the first, third,... lines the higher set of terms, respectively.

This division into two sets can be explained in the following simple way. The low terms of an energy diagram correspond to a configuration of the most stable electron "orbits," i.e., of type s and d; in other words they are obtained by adding s or d electrons, whereas the higher terms are generated by an addition of a p electron to the low energy states of the preceding ion. Thus terms of the same l value may arise from s and d electrons alone or else from d and one p or from d, s and one p electrons but they may be different by only one unit azimuthal quantum number.

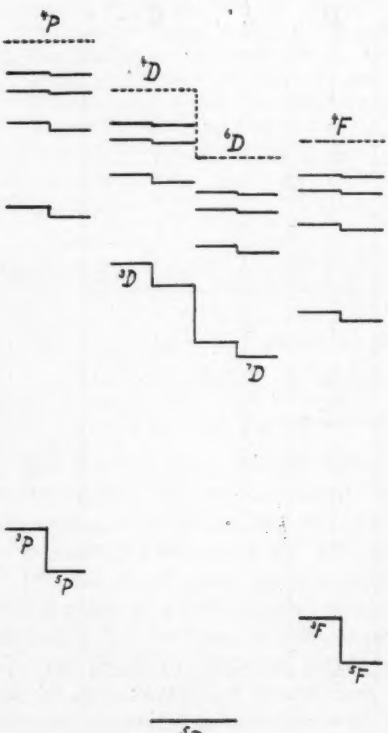


FIGURE 2

The lowest term in the iron arc spectrum is a ^5D—a result firmly supported by experimental facts and theoretical reasons[11]—followed by quintet and triplet P and F terms. It is worth noticing that there is no low ^3D appearing near ^5D.

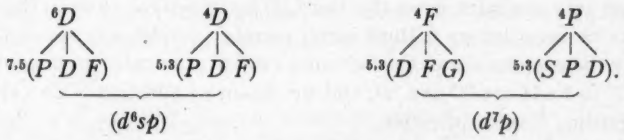
The terms of the second set appear in typical triads, indicated by dotted lines. Two triads consisting of terms with the same l values but different multiplicity, always appear together. Groups $^{7,5}(P\ D\ F)$, $^{5,3}(P\ D\ F)$ and $^{5,3}(D\ F\ G)$ are recognizable. The analysis of the spectrum, which is obviously getting more difficult for higher terms, has not so far advanced as to permit the allocation of the high ^5S and ^5P terms into triads.

D and F terms of a very high third set combining like the first have also been found; they are of special importance for the following. Unfortunately, their combinations are so weak and inconspicuous that it will be very difficult to complete this set of terms.

For the theoretical interpretation it is important to know the preceding spark spectrum, viz., Fe II, which has been investigated by H. N. Russell.[12]

For our purpose we need only a few of the lower terms. The normal state is a ^6D, then follow ^4F, ^4D, ^4P. ^6D and ^4D result from the configuration (d^6s^1); ^4F and ^4P come from (d^7).

Addition of a p electron to these furnishes the terms of the second set according to the following scheme:



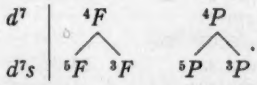
The first six triads are readily identified with those marked on figure 1. The ^5S term comes from ^4P and thus belongs to (d^7p). Indications of other terms belonging to this triad have been found.

The terms of the low and of the very high set originate from the above-mentioned terms of the spark by addition of d and s electrons, the former by the addition of 3_3 and 4_1, the latter of 4_3 and 5_1 electrons. For the third set this addition may be carried out according to the usual vector inequalities which were used by Russell and Saunders,[13] whereas for the low metastable terms Pauli's equivalence principle must be taken into consideration.

Let us now consider the low terms. The following electron configurations and spectral terms have to be expected:

d^6s^2	$^5D\ ^3H\ldots\ldots$
d^7s	$^5F\ ^3F\ ^5P\ ^3P\ldots\ldots$

All these terms have actually been found. The F and P terms readily show their origin in a configuration with *one* s electron: always *two* close lying terms appear, having the same l value, but different multiplicities. They result from the addition of an s electron (4_1) to the above-mentioned ^4F and ^4P terms in the spark:



We should also have rather high terms, with the same combination properties, corresponding to an addition of s electrons with higher total quantum number; in other words we may expect four series of F and P terms, which in pairs converge to the generating spark terms ^4F and ^4P. Thus we assert, and shall prove later, that the terms ^5F and ^3F at about 49,000 cm.$^{-1}$ are the second members of a sequence of ^5F and ^3F terms, approaching ^4F.

The ^5D is the only prominent representative of the configuration (d^6s^2); it may be regarded as the result of the addition of an (equivalent) s electron

(4_1) to (d^6s^1). The second (unprimed) ^5D term is situated much higher, at about 45,000 cm.$^{-1}$, and must be regarded as the second member of a term sequence in ^5D, as was first pointed out by Gieseler and Grotrian.[14] But a third, still higher ^5D term, in figure 1 at 52,000 cm.$^{-1}$, was published soon after by Meggers.[15] Gieseler and Grotrian's beautiful result now became very doubtful, since this third ^5D lay much too close to the second one to be regarded as a third series member. With the aid of the new theory the explanation of this becomes evident; the most prominent terms of (d^7s) in Fe II are ^6D and ^4D; and we obtain by addition of an s electron, disregarding Pauli's principle:

Fe II: d^7s	^6D		^4D
Fe I: d^7s,s	^7D	^5D	^5D ^3D .

This ordinary vector addition is, of course, only allowed provided the total quantum of the s electron is >4. Whereas among the low terms we have only *one* ^5D (viz., the lowest term of Fe), we will obtain *four* D terms of multiplicity 7, 5, 5, 3 among the higher terms. This is actually the case, as a glance on figure 1, shows. The two high ^5D terms thus become second members of two series, one converging to ^6D and the other to ^4D. Quantitative proof will be given below.

The dropping out of the ^7D term at the low total quantum numbers is a direct consequence of Pauli's equivalence principle, and as such entirely similar to the dropping out of the ^3S at lowest values of n in the spectra of the alkaline earths, as was pointed out by the author[16] in 1924.

The very high ^3D term at 54,000 cm.$^{-1}$ was not given before. Since it is of importance for the identification of all these four D terms as (d^7s, s) to prove the existence of ^3D, its combinations with two second set terms, viz., a^3F and b^3D' are given below:

		^3D		
		53747.45	54066.80	54386.10
a^3F	31307.27	22440.18		
		4455.037 (2*u*)		
	31805.10	21942.35	22261.70	
		4556.128 (3)?	4490.768 (2*u*)	
	32134.02	21613.43	21932.78	22252.08
		.....	4558.110 (1)	4492.693 (1*u*)
b^3D	38175.38	15572.07	15891.42	
		6419.988 (3*u*)	6290.968 (3*u*)	
	38478.07	15069.38	15388.73	15708.03
		.....	6496.62 (3)	6364.384 (1)
	38995.77		15071.03	15390.33
			.....	6495.796 (2)

This ^3D furthermore combines in three lines with a^3D and with b^3F of the second set.

Figure 2 illustrates more closely our identifications of the terms of Fe I and their way of approaching the low terms of Fe II. The terms of the second (middle) set are not drawn in, as no higher series members with 5_2, etc., electrons are known.

The crucial test is obviously the Rydberg formula. Since we know the differences between the spark terms, i.e., between the series limits, we have more empirical data than available constants. We shall work only with the sublevels of each term which has the highest j value.

(1) D series:

(α) a^5D and b^5D; Gieseler-Grotrian series.

(In the author's old notation d^1 and d^2, in that of Meggers A and T.)

$$a^5D_4 - b^5D_4 = 44{,}677.$$

Hence $a^5D_4 - {}^6D_5^+ = 65{,}523$ Rydberg corr. $\mu = 0.294$

(β) a^5D and c^5D (in the notation of Meggers A and T')

$$a^5D_4 - c^5D_4 = 51{,}350$$

$$a^5D_4 - {}^4D_4^+ = 73{,}587 \qquad \text{Rydberg corr. } \mu = 0.221$$

(2) F series:

(α) a^5F and b^5F (in the old notation of the author $\bar{f}^1$ and $\bar{f}^2$, in that of Meggers B and U),

$$a^5F_5 - b^5F_5 = 40{,}077$$

$$a^5F_5 - {}^4F_5^+ = 59{,}880 \qquad \mu = 0.353.$$

a^3F and b^3F. (In the author's notation a^3F is $\bar{F}^1$, in that of Meggers C.) The term b^3F was not known before; the author predicted its position according to the above-explained ideas. The new term, b^3F, combines with almost every term of the second set, always giving weak lines; for its proof only the combinations with ^3G and with a^3F may be given

		^3F		
		47960.89	48531.82	48928.33
^3G	35379.23	12581.66		
		7945.89 (7)		
	35767.59	12193.30	12764.23	
		8198.97 (2)	7832.24 (6)	
	36079.39	11881.6	12452.40	12848.94
		.....	8028.37 (2)	7780.65 (5)
b^3F	36686.20	11274.74	11845.62	
		8866.94 (3)	8439.58 (3)	
	37162.76	10798.13	11369.06	11765.57
		9258.49	8793.37 (2)	8497.00 (2)
	37521.18		11010.64	11407.15
			9079.63	8763.97

Since the term value of a^3F_4 with respect to a^5D_4 is 11,976, the distance between the two alleged series members becomes 47,961 − 11,976 = 35,985.

$$a^3F_4 - b^3F_4 = 35{,}985$$

$$a^3F_5 - {}^4F_5^+ = 54{,}767 \qquad \mu = 0.415.$$

We have now obtained in four independent ways the distances of various arc and spark terms. By means of an application of the combination principle these distances can be reduced to the first ionization potential, namely, $^5D_4 - {}^6D_5^+$. Figure 2 will illustrate this procedure.

We obtain from (1α)

$$a^5D_4 - {}^6D_5^+ = 65{,}523.$$

According to Russell's analysis of Fe^+, we have

$${}^6D_5^+ - {}^4D_4^+ = 7955$$

hence from (1β)

$$a^5D_4 - {}^6D_5^+ = 65{,}632.$$

The third value is deducible from (2α) by means of the term difference in the arc spectrum

$$a^5D_4 - a^5F_5 = 6928$$

and one in the spark spectrum (Russell):

$${}^6D_5 - {}^6F_5 = 1873$$

we thus obtain:

$$a^5D_4 - {}^6D_5^+ = 64{,}935.$$

The term sequence in $^3D_3$ approaches the same limit $^6D_5^+$, as an application of Pauli's coördination rule shows. We obtain from (2β), since the arc spectrum term difference

$$a^5D_5 - a^3D_4 = 11{,}976$$

a fourth value

$$a^5D_4 - {}^6D_5^+ = 64{,}870.$$

We may take as unweighted mean 65,240 which corresponds to an ionization of 8.06 volts.

We wish to leave undecided whether the above agreement of four independently obtained values is an argument against Gieseler and Grotrian's value 65,994 ± 20 cm.$^{-1}$, and consequently against their third member of the series. In general we arrive at a confirmation of their idea about series in Fe.

The whole method resembles very much that applied by C. C. Kiess

and the author[17] to the spectra of Cr, with the only difference that in Fe the spark spectrum is sufficiently investigated (Russell), whereas in Cr the discovered series regularities were used to find the normal state of Cr^+.

Figure 2 shows how this procedure can be extended and how more series may be found. Thus two P terms will occur, which, together with the two low terms ^5P and ^3P at 20,000 form a series converging to $^4P(d^7)$. It is interesting to note in this connection, that since $^5F - {}^5P$ is almost equal to $^4F - {}^4P$ the sequence n^5P will have the same Rydberg correction as has n^5F.

We are in agreement with a rule brought forward by Kiess and the author that the transition from arc to spark spectrum is always caused by a loss of an s electron,[18] and furthermore confirm our identification of the k values of the terms in Fe I and Fe II, which to a certain extent deviated from that of Hund. Hund ascribed the ^4F and ^4P terms in Fe II, whose existence he was forced to assume from the second set terms of the arc spectrum, to the configuration (d^6s) instead, as we did, to (d^7). The occurrence of terms belonging to the type (d^z)—z being the number of valence electrons—is an interesting and common phenomenon in first spark spectra; in several (e.g., Cr^+, V^+, Cu^+?) they even exceed the terms of the other types, $(d^{z-1}s)$ and $(d^{z-2}s^2)$, in stability, and furnish the normal state.

[1] Published by permission of the Director of the Bureau of Standards.

[2] F. M. Walters, *J. Opt. Soc.*, **8**, 245, 1924.

[3] O. Laporte, *Zs. Physik*, **23**, 135; **26**, 1, 1924.

[4] H. N. Russell and F. A. Saunders, *Astrophys. J.*, **61**, 38, 1925.

[5] F. Hund, *Zs. Physik*, **33**, 345, 1925.

[6] W. Pauli, *Zs. Physik*, **31**, 765, 1925.

[7] W. F. Meggers, *Astrophys. J.*, **60**, 60, 1924.

[8] W. Grotrian, *Naturwissenschaften*, 1925.

[9] O. Laporte, loc. cit.[3]

[10] H. N. Russell, *Science*, 1924. From today's theoretical viewpoint this distinction appears as the only justified one. One should denote the terms of the second set, e.g., by a dot or circumflex, and abolish the dashes and primes entirely.

[11] O. Laporte, *Nature*, May 22, 1926.

[12] H. N. Russell, *Astrophys. J.*, **61**, 1925; *Mount Wilson Contrib.* No. **286**, page 52. The writer is deeply indebted for the permission of using all his unpublished material on Fe II.

[13] H. N. Russell and F. A. Saunders, *Astrophys. J.*, **61**, 60, 1925.

[14] Gieseler and W. Grotrian, *Zs. Physik*, **25**, 165, 1924.

[15] W. F. Meggers, loc. cit.[7]

[16] *Zs. Physik*, **26**, 1, 1924, vide page 18.

[17] C. C. Kiess and O. Laporte, *Science*, **63**, 234, 1926.

[18] Loc. cit.

THE LOCATION OF THE ELECTROMOTIVE FORCE IN A PHOTO-ACTIVE CELL CONTAINING A FLUORESCENT ELECTROLYTE

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Communicated June 26, 1926

Early investigators[1,2] of the electromotive force produced by the illumination of an electrolytic cell which contains a fluorescent electrolyte have reported that it was necessary to illuminate the actual boundary between the electrode and the solution in order to get the effect. Recently Grumbach[3] found that if sufficiently dilute solutions are used an electromotive force may be obtained when the light does not fall on the electrode. He attributes this to a photo-chemical change in the electrolyte which makes the cell in effect a concentration cell and he finds that the total electromotive force observed when the electrode is illuminated is the superposition of this effect and an electromotive force in the production of which the electrode is directly concerned. He attributes Goldmann's[2] failure to find the effect to the fact that the concentration of his solutions was so large that the active light was absorbed in a very thin layer at the surface.

Goldmann used as electrodes semi-transparent platinum films deposited on the glass walls of the cell and he illuminated the cell through one of the electrodes. He used concentrated alcoholic solutions, the fluorescent dyes being as a rule much more soluble in alcohol than in water. It seems desirable to look for evidence of the effect described by Grumbach using Goldmann's type of electrode and strong solutions.

If the electrolyte is made to flow along the surface on which the electrode is deposited and may be illuminated before it reaches the electrode, through the electrode or after leaving it, at will, evidence of an electromotive force due to a photo-chemical change in the solution should be obtainable even if the depth of penetration of the active light is very small. This has been accomplished by placing the solution in a dark glass bottle of square cross-section, mounted upon a turn table so that it can be rotated in either direction about its central vertical axis. The electrodes were deposited by cathodic sputtering on the opposite sides of a glass test tube somewhat smaller than the neck of the bottle. The test tube is slipped over a brass tube and held in place by the friction of a thin layer of felt. The brass tube is fixed rigidly, coaxial with the axis of rotation of the bottle with the electrodes immersed in the solution. If this adjustment is accurately made, the liquid in a thin layer near the test tube will stream through a circular path along the surface of the tube.

The light from a concentrated filament 100-watt lamp passes down

through the brass tube and is reflected by a mirror near the bottom of the tube so as to pass horizontally through a window cut in the wall of the tube. This window is slightly larger than the electrode. The test tube is free to turn upon the axis of the brass tube. A lever and circular scale at the top of the test tube make it possible to put one of the electrodes in the beam of light from the window or in any desired angular position with reference to it. Connection to the electrodes is made by heavily sputtered platinum strips running up from the electrodes to the top of the test tube. To the upper ends of these are soldered fine copper wires. The strips are insulated from the solution by a thin coat of bakelite lacquer. A more detailed description of the apparatus will appear in a later article.

The current was measured by a galvanometer connected to the cell through a series resistance of 1.2 megohms. Any change in the condition of the cell starts a gradual variation of the current from the old to the new

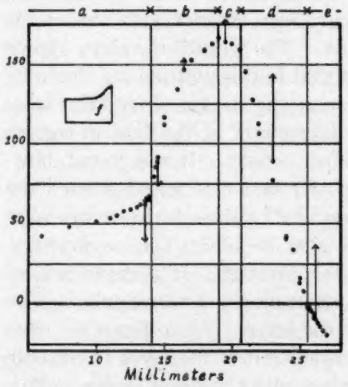

FIGURE 1

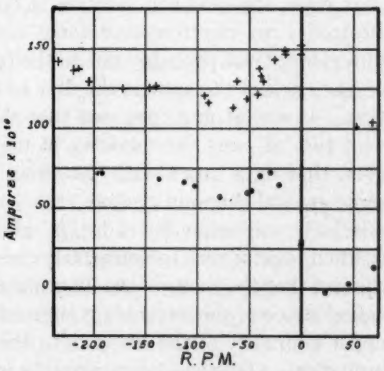

FIGURE 2

steady value. A 3 per cent solution of rhodamine-B in absolute alcohol was used. Mrs. Jenkins[4] has shown that at this concentration the cell has a maximum sensitivity to light and that the steady state is more promptly attained than at larger or smaller concentrations. This is an important consideration when a considerable number of observations are to be taken. In the work here described from 2 to 5 minutes were required for the current to become steady after each change in the condition of the cell.

In figure 1 are plotted the values of the current against the position of the electrode measured in millimeters displacement from an arbitrary zero position. The electrode was in the center of the beam of light at 19.8 mm. The semi-circumference of the test tube was 28 mm. For settings in the region "*c*" the electrode was completely bathed in light, in regions

"*b*" and "*d*" it was partly illuminated, in regions "*a*" and "*e*" the only light falling on the electrode was that due to scattering and fluorescence in the neighboring illuminated solution. During this experiment the rotation was kept constant at 38 revolutions per minute and the direction of rotation was such that when the electrode was in region "*a*" the fluid flowing by the electrode had recently passed in front of the window while, in region "*e*" the fluid was approaching the window. In taking the data shown, the electrode was not moved always in one direction but frequent large displacements were made to ensure that conditions were not changing with time. The six points shown at the origins of the arrows were taken at the end of the experiment. After taking each of these data the rotation was temporarily stopped and the current observed. The arrows indicate the change in the current produced by stopping the motion.

The difference in the results plotted in regions "*a*" and "*e*" shows definitely that the illumination of the solution produces some change such that when the modified solution is brought into contact with one of the electrodes an electromotive force results. The negative values shown in region "*e*" are probably due to the fact that in this position the electrode on the back of the tube is the first to receive the stream of modified solution. It was at first supposed that the asymmetry of the data in regions "*b*," and "*d*" was also evidence of the effect sought. It was found, however, that data taken with the direction of rotation reversed showed the same general shape in regions "*b*," "*c*" and "*d*" although the values were relatively somewhat lower in "*b*" and higher in "*d*." This asymmetry, is, then, partly due to something else than rotation. It is explained by the fact that the shape of the illuminated electrode is not rectangular. The actual shape of the electrode is shown by the insert, "*f*," in figure 1. The upper boundary of the electrode is the lower limit of the layer of bakelite insulation. This had been unevenly applied with the result shown. This pair of electrodes were remarkable in that the current, when the cell was not illuminated, was negligible. This condition is difficult to attain and, unless it is met, reproducible data such as here shown can rarely be obtained. No attempt was therefore made to repair the electrode.

In the first experiments performed with this apparatus the results differed from those shown in figure 1 in that no marked difference occurred between the values obtained in regions "*a*" and "*e*." These data were all taken with large rates of rotation. Studies of the variation of the current with speed were therefore made. Figure 2 shows two of these. The data represented by the crosses was made at scale setting 19.5 mm. and that, by the dots, at scale setting 13.5. These are the same settings as those represented by the arrows in regions "*c*" and "*a*" of figure 1. In the first case, the electrode is completely bathed in light, in the second, it is not directly illuminated, its nearest edge being 0.6 mm. from the beam of light.

In each case the change in the current as the value of the speed changes from −40 to about 0, agrees well with the results shown by the arrows in regions "*a*" and "*c*," figure 1. Between −40 and −50 r.p.m. there appears a marked decrease in the value of the current. This is found in both curves. It has been observed that the speed at which this break occurs depends upon the accuracy with which the test tube is centered with the axis of rotation.

It would seem that at this critical speed the flow ceases to follow regular stream lines and becomes turbulent resulting in a general stirring of the solution. This reduces the concentration of the product of the photochemical reaction at the face of the illuminated electrode in the first case and causes less of the product to reach the electrode in the second. The reason for the gradual increase of the current with further increase in the speed of rotation in both cases is not clear but it may be associated with the decrease in the polarization produced by stirring. This has been observed with the same apparatus in a series of experiments which will be described elsewhere.

In the case of the second of these curves the current decreases as the speed changes from small negative to small positive values becoming negative at about 20 r.p.m. but again becoming positive at the critical speed.

The positions of the arrows in regions "*a*" and "*e*," 13.5 mm. and 26.1 mm., are symmetrical with respect to the center of the window. It is observed that the points of the arrows at these positions indicate approximately the same current. This shows that the difference in the effects observed at these points is the result of rotation and not stray light. This is also evidenced by the agreement between the small negative current shown in figure 2 for a rotation of +38 r.p.m. at the position, 13.5 mm. and that shown in figure 1 for −38 r.p.m. at the position, 26.1.

These data indicate that the photo-active electromotive force in the Goldmann cell is in part due to action by light on the fluorescent electrolyte in which the electrode plays no active part. Concerning a possible electromotive force in the production of which the illumination of the electrode is necessary, the results are not so conclusive. It should be noted, however, that the curve of figure 1 has sudden changes in the value of its slope at the boundaries of regions "*a*" and "*b*," and of regions "*d*" and "*e*," where the electrode is unilluminated but has one edge at the edge of the window. In both cases this is in the direction of an increase of current as the electrode becomes illuminated. The intensity of the light falling on the solution through the electrode is less than that which falls directly because of the absorption of the electrode. If the electrode were not directly concerned in the production of an electromotive force one might expect in passing from region "*a*" to "*b*" a decrease in the current. This part of the curve has been carefully examined for such an effect with negative results.

[1] Hodge, *Physic. Rev.*, **26**, 540 (1908); **28**, 25 (1909).
[2] Goldmann, *Ann. Physik*, **27**, 449 (1908).
[3] Grumbach, *Comptes Rendus*, **176**, 88; **177**, 395 (1923); **179**, 623 (1924); and **180**, 1102 (1925).
[4] *Physic. Rev.*, **18**, 402 (1921).

REMARKS ON PROFESSOR LEWIS'S NOTE ON THE PATH OF LIGHT QUANTA IN AN INTERFERENCE FIELD

By Richard C. Tolman and Sinclair Smith

Norman Bridge Laboratory of Physics and Mount Wilson Observatory

Communicated July 12, 1926

In an earlier number of these PROCEEDINGS,[1] Professor G. N. Lewis adopted an extreme form of the light quantum theory, in which the light quanta are assumed to travel in straight lines except when deflected by matter, the facts of interference being explained by the assumption that the quanta do not go to those places where the wave theory forbids the action of radiation. As a crucial test between this and other theories of light, Professor Lewis proposed an experiment in which the absence of light quanta, traveling over a particular path which leads to the center of of an interference band on a screen, would produce an unbalanced torque on a reflecting mirror.

In criticizing this proposed test,[2] the present authors called attention to the fact that the absence of action at a given point certainly could not always be interpreted as due to the absence of quanta passing through that point, since it would then be impossible to account for the well known phenomena of standing light waves. For this reason we suggested that even if light quanta should travel in straight lines, Professor Lewis's experiment might give no effect, since quanta might still be traveling through the point on the screen where interference exists, and then continue by transmission or reflection to places where the action of light is permitted.

Professor Lewis now replies[3] that our suggestion would contradict the principle of the conservation of energy. He argues that, if the interference pattern falls on a screen of highly absorptive material, all the energy available from the light source will produce its effect in a very thin layer of the screen at those places where the light bands are produced by reinforcement, and hence there can be no additional quanta traveling through the position of the dark bands.

We are, however, unable to agree with this argument. In discussing the case of an absorptive screen we called attention to the possibility that quanta arriving on the screen at a position where interference occurs could

be deflected, if necessary, to regions where the action of light is permitted by the wave theory; and in the case of a *highly* absorptive material it would seem reasonable to expect a very sharp deflection of the quanta, that arrive at points where interference occurs, to neighboring regions where they are needed to produce the experimentally verified reinforcement. Hence we do not agree that our suggestion involves any contradiction to the principle of the conservation of energy.

In conclusion we wish again to emphasize our belief that hybrid theories containing disparate elements taken both from the wave theory and corpuscular theories of light are probably temporary expedients which will later give place to an integrated view.

[1] G. N. Lewis, these PROCEEDINGS, **12**, 22 (1926).
[2] Tolman and Smith, *Ibid.*, **12**, 343 (1926).
[3] G. N. Lewis, *Ibid.*, **12**, 439 (1926).

THE MEAN FREE PATH OF ELECTRONS IN MERCURY VAPOR

BY L. R. MAXWELL

DEPARTMENT OF PHYSICS, UNIVERSITY OF MINNESOTA

Communicated July 6, 1926

Numerous investigators[1] have determined the nature of the scattering of electrons in many of the common gases and have interpreted their results in terms of the mean free path of the electron. The present article describes a method for measuring the mean free path of electrons and presents the results for mercury vapor for velocities ranging from a fraction of a volt to 3000.

We know from kinetic theory that for a beam of electrons moving through a gas

$$I = I_0 e^{-x/\lambda} \qquad (1)$$

where I_0 is the initial number of electrons in the beam, I the number which go a distance x without suffering a collision with a molecule of the gas and where λ is the mean free path. In order to apply this equation experimentally it is sufficient to insert a movable Faraday cage which can measure the current I_0 and then the succeeding values of I. In doing this the natural spreading of the beam must be considered. When there is no gas in the presence of the electrons, let K be the fractional part of the total number of electrons initially present in the beam which enter the cage opening for a certain position x. With this definition of K our above equation becomes

$$I = KI_0 e^{-x/\lambda} \qquad (2)$$

which presents a working formula. Having obtained K for a value of x

with the gas absent and having found I/I_0 for the same x with the gas present, λ can then be computed.

Figure 1 shows diagrammatically the apparatus and electrical circuit. Electrons from the heated tungsten filament F were sent through circular openings S_1, S_2, S_3 and S_4. S_1 and S_3 were 2 mm. in diameter and 2 cm. apart. S_2 was 4 mm. in diameter and midway between S_1 and S_3. S_4 was 1 mm. from S_3 and 4 mm. in diameter. Thus a beam of electrons was obtained in the equipotential region C_2. All of the electrons leaving S_3 were measured by galvanometer G_2. The Faraday cage C_1 was a complete absorber of electrons because of its extreme length 21 cm. and its width 4.5 cm. Circular openings D_1 and D_2 were of 14 and 12 mm. diameter, respectively. Therefore, once an electron passed through D_2 it was measured by galvanometer G_1 as is shown in figure 1. The cage was moved through a distance of 8 cm. by a windlass, and the scattering of the electrons from the beam would appear as a change of the current through G_1. The cage was made of copper, the other parts of iron, with the exception of a nickel gauze G, which decreased the reflection and secondary emission of electrons from the walls of C_2. Additional precautions were taken to reduce the presence of secondary electrons by nickel plating all of the metal parts, leaving the surfaces with a dull finish.[2] The parts were thoroughly outgassed in a vacuum furnace to remove all occluded gases.

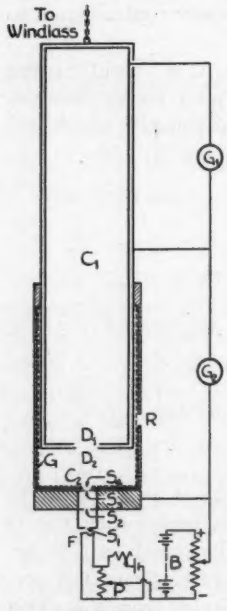

FIGURE 1
Apparatus and electrical circuit.

The position for $x = 0$ was taken when the cage was resting directly over S_4. Galvanometer G_1 gave the total number of electrons I_0 initially present in the beam. Simultaneously G_2 should have read the same as G_1, but generally indicated slightly more current than did G_1, because of a few electrons that would drift over to the edges of the opening S_4 and not enter C_2. In each instance the difference was noted so that G_2 could be read in terms of G_1 giving continually the term I_0 while at the same time I would be read by G_1 for six different settings of the cage (i.e., for $x =$ 3, 4, 5, 6, 7 and 8 cm.).

Figure 2 gives the velocity distribution of I_0 for accelerating potentials of 5, 10 and 40 volts, and shows more secondary electrons present for the 40 volts than for the other two voltages. This is due to the secondary emission from the edges of S_1 and the other openings.

With the pressure in C_2 less than 10^{-6} mm. Hg, the values of K were obtained for the various settings of C_1, and for the different accelerating potentials. The mercury vapor was then introduced at a definite pressure. The temperature of the tube containing the apparatus was kept at 27°C. and hence the pressure in the tube was that corresponding to this temperature which is 2.9 bars.[3] Because of the heating due to the filament the actual temperature of region C_2 was 75°C., with a slight temperature gradient from $x = 0$ to $x = 8$ cm. The mean free path of the mercury molecule was large compared to the openings leading from C_2 to the cooler part of the tube, so that the ratio of the pressures in the two parts is equal to the square root of the ratio of the absolute temperatures, which gives the pressure in C_2 as 3.12 bars. With this pressure and temperature the

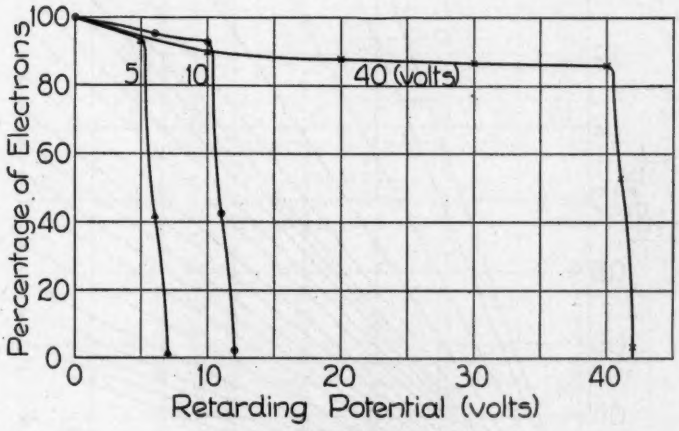

FIGURE 2
Velocity distribution of I_0.

ratio of I/I_0 was found. The order of magnitude of I_0 was 2×10^{-8} amperes, and variations of I_0 by more than 200% caused no change of I/I_0. The solution for λ was performed graphically by plotting $-\log_e(I/KI_0)$ with respect for x, and the inverse of the slope of the curve gave the mean free path.

Figure 3 shows $-\log_e(I/KI_0)$ plotted with respect to x for a number of velocities. It is noticed that the points form straight lines showing that there is a linear relation between $-\log_e(I/KI_0)$ and x, which is in accord with our equation (2). Because of the solid angle that is subtended by D_2 it would be possible for an electron after colliding to still pass through D_2 and be measured as having not collided. The magnitude of this effect can be calculated and it is found that it would cause an error of 1% in

the results shown in figure 3, which is approximately the order of experimental error.

Figure 4 gives the results found for the mean free path of the slow electrons at a pressure of 3.12 bars and temperatures of 75°C. A change in the direction of the curve occurs at 4.9 volts, and a very slight indication of a change in slope takes place at 6.7. The change at 4.9 is more notice-

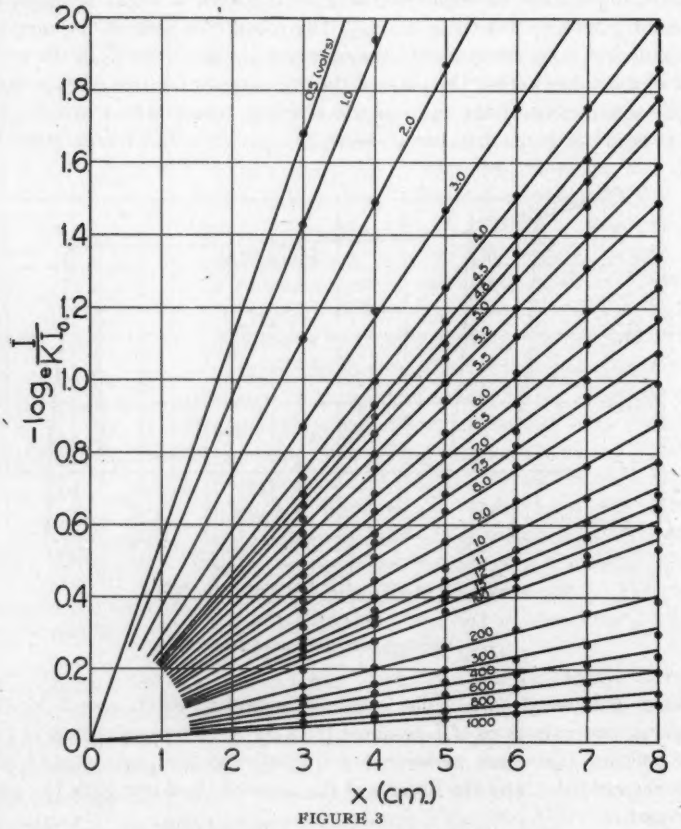

FIGURE 3

Showing linearity between $-\log_e\left(\frac{I}{KI_0}\right)$ and x.

able than that at 6.7, which is to be expected because the collision at 6.7 is known to be less prominent than at 4.9. This shows that the mean free path is affected by the type of collision which occurs at these critical potentials. Figure 5 is a continuation of figure 4 showing results for higher velocities. A decrease in the curve is found with a minimum at about 40

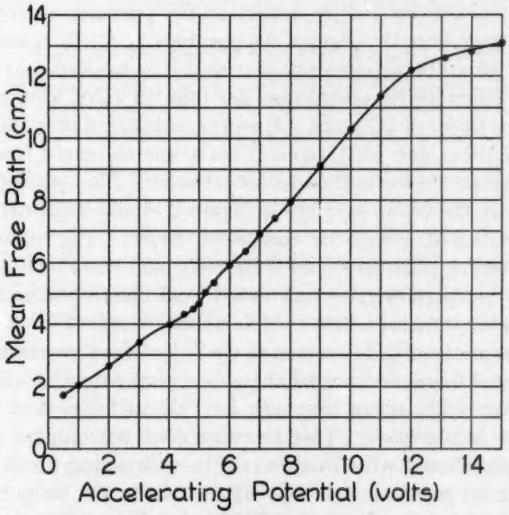

FIGURE 4

Mean free path for the lower voltages at pressure of 3.12 bars and temperature 75°C.

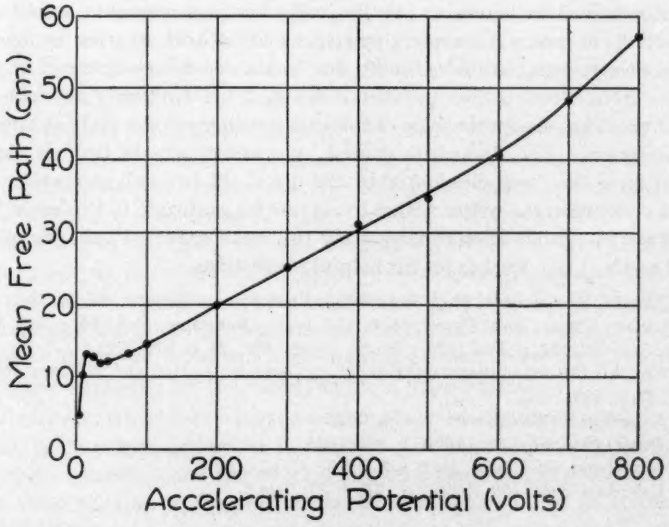

FIGURE 5

Mean free path for the higher voltages at pressure of 3.12 bars and temperature 75°C.

volts. This is due for the most part to the presence of slow secondary electrons coming from the edges of the openings S_1, S_2, S_3, S_4 and D_2. From figure 2 for 40 volts' accelerating potential it is noticed that about 15% of the total electrons have velocities less than 40 volts, in fact, 7.5% have an average velocity of 2.5 volts. It can be calculated that the short mean free path of these slow electrons will cause the measured free path at 40 volts to be about 8% lower than its actual value. This percentage of error will be less at the lower voltages as figure 2 would indicate, but at the higher velocities it would be somewhat larger. The mean free path was measured for 1120, 2040 and 3050 volts, and was found to be 73, 123 and 144 cm., respectively. λ calculated from kinetic theory for this pressure and temperature is 21.5 cm., which is that given for 230 volts in figure 5.

Brode[4] has measured the scattering coefficient for slow electrons in mercury vapor and found no unusual changes at the critical potentials, and no small increase of the mean free path for velocities less than one volt, as reported by Minkowski.[5] This increase does not appear in figure 4 which is in agreement with Brode's results. Changing Brode's coefficient of scattering for pressure of 1 mm. Hg at 0°C. to the mean free path for pressure of 3.12 bars at 75°C. it is found that his results are of the same order of magnitude as those given in figure 4. For example, he obtains 5 cm. for 4 volts which is compared with 4 cm. from figure 4. His results, however, for the higher velocities give a much longer mean free path than is shown in figure 5. At 100 volts his measurements would give $\lambda = 47.3$ cm. which is considerably larger than 14.5 cm. as given by figure 5. This disagreement is undoubtedly due to the secondary emission of electrons from Brode's two parallel disks and his circular ring collector. Lawrence[6] has shown the type of collector which gives complete absorption of electrons. The difficulties caused by space charge in Brode's experiment have here been eliminated by the use of the two galvanometers.

In conclusion the writer wishes to express his gratitude to Professor John T. Tate who in addition to suggesting this work rendered valuable advice and to Dr. J. W. Buchta for his helpful suggestions.

[1] Lenard, *Ann. Physik*, **12**, p. 714, 1903. Compton and Benade, *Physic. Rev.*, **8**, p. 449, 1916. Mayer, *Ann. Physik*, **64**, p. 451, 1921. Ramsauer, *Ibid.*, **64**, p. 513, 1921; **66**, p. 546, 1921; **72**, p. 345, 1923. Brode, *Physic. Rev.*, **25**, p. 636, 1925.

[2] For this method of diminishing secondary electrons see Hull and Williams, *Physic. Rev.*, **27**, p. 435, 1926.

[3] Langmuir, *General Electric Review*, 1924.

[4] Brode, *Proc. Roy. Soc.*, **109A**, p. 397, 1925.

[5] Minkowski, *Zs. Physik*, **18**, p. 258, 1923.

[6] Lawrence, *Proc. Nat. Acad. Sci.*, **12**, p. 29, 1926.

THE ORGANIC CONTENT OF LAKE WATER

BY EDWARD A. BIRGE AND CHANCEY JUDAY

WISCONSIN GEOLOGICAL AND NATURAL HISTORY SURVEY

Read before the Academy November 11, 1925

For many years the Wisconsin Geological and Natural History Survey has been investigating the lakes of the state. The complex life of lakes offers a great variety of interrelated problems for study, each of which demands at least some attention before any general conclusions can be reached. Thus the work has advanced slowly and in a more or less piecemeal fashion, according as opportunity allowed.

Many aspects of limnology have been treated in the bulletins of the Survey and in briefer publications. The morphometry of the lakes has been presented in two bulletins. The principal systematic studies have included two bulletins on the plankton algae; a study of the insects of Lake Mendota; and a monograph on the Rotifera, of which three parts with 88 plates have already appeared. To the physics of the lakes the Survey has contributed a bulletin on the dissolved gases and papers on temperatures and on the absorption of the sun's radiation. But the main continuous work has been on the organic life of the lakes, both as to quantity and chemistry. The bottom fauna and the annual crop of higher plants have been studied from these points of view; and two bulletins have been published on the quantity and chemistry of the plankton, besides numerous papers dealing with special chemical problems of the plankton and with the nitrogen dissolved in the water.

The present paper brings together the results of four studies, of which two have been published and two are here reported for the first time. It states the content of organic matter in lake water, including that organized into plants and animals, or existing in the form of organic debris, or held in some sort of solution. For this purpose are employed a report of Birge and Juday[1] on the plankton, a report by Domogalla, Juday and Peterson[2] on the soluble nitrogen; and hitherto unpublished studies of the organic carbon and the ether extract found in the dry residues of evaporated lake water. The result is to furnish the beginnings of an inventory of the fundamental food supply for the living beings of inland lakes.

The observations here reported were made on large samples of lake water, whose average size was about 100 liters. The plankton was extracted by Sharples centrifuge and the water was then evaporated in a vacuum pan. The total amount of dry residue was determined and also its content in organic nitrogen and organic carbon. Fifty such samples were examined from Lake Mendota and 24 from 15 other waters. The determinations

of soluble nitrogen give the total amount of organic nitrogen and its division into free amino, peptide and non-amino nitrogen.

The organic carbon was determined from 28 of these residues, 14 from Lake Mendota and 14 from 12 other lakes. The ether extract was obtained from six single samples, four from Mendota and two from other lakes; and also from two large composite samples, one made up from ten residues from the surface water of Mendota and the other from six residues from bottom water.

The results of these determinations may be stated directly as milligrams of organic carbon and organic nitrogen per liter of lake water; and the organic matter represented by these elements may be computed by standard processes.

DISSOLVED ORGANIC NITROGEN AND ORGANIC CARBON

Milligrams per liter of water

	NITROGEN			CARBON		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
Lake Mendota, 14 cases	0.289	0.559	0.393	4.00	7.95	5.80
Other lakes, 14 cases	0.143	0.750	0.460	3.02	13.22	6.66

The ratio of nitrogen to carbon in Lake Mendota ranged from 1 to 9.1 as a maximum to a minimum of 1 to 20.6, with a mean value of 1 to 14.8; in the other lakes the ratio was: maximum 1 to 9.6, minimum 1 to 27.0, mean 1 to 14.3.

This nitrogen and carbon is called "dissolved," a term which is by no means exactly applied. A small part is no doubt present in minute organisms and organic particles; most of it probably exists as colloids; some of it is in true solution.

The amount is far greater than that which is found in the plankton, including in that term both organisms and organic matter removed from the water by the centrifuge. The water of Lake Mendota yields, as an average, about 0.140 milligram of plankton nitrogen per liter of water; and slightly less than 1.00 mg. of plankton carbon. These quantities are much smaller than those of the dissolved organic matter and there is a higher ratio of nitrogen to carbon. These data for plankton come from the report of Birge and Juday and relate to the average of a series of observations extending over more than two years.

The dissolved organic matter represented by the organic nitrogen and carbon may be computed. Crude proteins are estimated by the standard formula, $N \times 6.25$. Organic carbon is distributed on the basis that proteins contain 53% of carbon, fats 75% and carbohydrates 45%. If the ether extract has not been determined all of the non-nitrogenous carbon must be computed as carbohydrate. This is the case with most of the lakes other than Mendota and the method causes an excess error of about 3% of the total organic matter.

Thus it appears that Lake Mendota maintains a standing crop of organic matter amounting to nearly 15 mg. per liter of water. If the smallest and the largest amounts as yet observed in each class of compounds are put together, the minimum would be 9.1 mg. (plankton 0.69 mg., dissolved 8.41); the maximum would be 20.45 mg. (plankton 3.33 mg., dissolved 17.12 mg.). On the average, the organic matter of the plankton is less than one-sixth of the organic dissolved matter; the plankton proteins are about one-third of the dissolved proteins; the fats are about one-fourth and the carbohydrates little more than one-tenth of the corresponding dissolved substances. The percentage of proteins in the plankton is twice as great as in the dissolved matter; the percentage of fats is nearly as large; and the carbohydrate content of the dissolved matter is correspondingly higher than that of the plankton.

TOTAL ORGANIC CONTENT OF THE WATER OF LAKE MENDOTA

Milligrams per liter

		WEIGHT		PER CENT
Plankton 87 samples	Crude protein	0.88		44.5
	Fats	0.15		7.5
	Carbohydrate	0.95	1.98	48.0
Dissolved 20 samples	Crude protein	2.76		21.9
	Fats	0.56		4.4
	Carbohydrate	9.27	12.59	73.7
	Total		14.57	

In the 12 lakes other than Mendota the total dissolved matter ranges from 6.35 mg. per l. to 28.81 mg. per l. with a mean of 14.27 mg. The relations of plankton to dissolved matter and of nitrogenous to non-nitrogenous substances show wide variation in single cases, both in Mendota and the other lakes, but the average results are much the same.

The main source of the dissolved organic matter is the plankton, although there are contributions from the higher plants of the lake and from inflowing waters. In Lake Mendota the total *annual* crop of organic carbon contained in the higher aquatic plants is not one-third of the average *standing* crop of dissolved organic carbon. In other lakes the possible contribution from the higher plants may be even smaller and in Lake Michigan it must be quite negligible. The same general statement is to be made for organic material brought in by affluents, though the quantitative relation has not been computed.

No special chemical studies have been made on either the carbohydrates or the fats of the dissolved matter, but under the microscope its fats appear like those of the plankton. The nitrogenous compounds of the plankton, however, can be compared with those of the dissolved matter.

It thus appears that the percentile distribution of the organic nitrogen is practically identical in the plankton and in the residues. There have also been found in the residues from Lake Mendota and from other lakes those amino acids which are indispensable in food, such as tryptophane, cystine, tyrosine, histidine and arginine.[3] We have therefore direct chemical evidence for the statement that the proteins of the dissolved organic matter have the same food value as those of the plankton. We may also say that the fats of the two classes of organic matter have an equal food value; and the statement may be extended to the carbohydrates, although our knowledge is least for this class of compounds whether in plankton or in solution.

PERCENTILE DISTRIBUTION OF FORMS OF ORGANIC NITROGEN

	LAKE MENDOTA		12 OTHER LAKES
Nitrogen	Plankton	Residues	Residues
Free Amino	17.3%	20.3%	17.2%
Peptide	41.7	39.3	38.7
Non-amino	41.0	41.4	44.1
	100.0	100.0	100.0

Those who have investigated the organic content of sea water agree in finding the amount very small, the total amount being one to three milligrams per liter of water. Moore[4] (p. 269) sums up the facts for the dissolved carbon in the words: "The organic carbon dissolved in sea water is an exceedingly minute quantity lying at the limits of detectability by the best known methods." The question, therefore, of the nutrition of marine plankton has called for the determination of quantities of organic matter so small as to be close to the limit of the errors of observation. It has been correspondingly difficult to decide whether the marine plankton constitutes a self-sustaining community of eaters and eaten.

The results here reported show that the situation in fresh water lakes is very different. The quantity of organic material is far greater than in sea water and the quantity of inorganic salts is far smaller. There is in the water a large standing crop of organic matter outside of the plankton; and this is ordinarily several times and often many times greater than that in the plankton, so far as this can be removed from the water by centrifuge or by Berkefeld filter. This dissolved organic matter is apparently as well suited for food as is the organic matter of the plankton.

The main groups of eaters in the plankton are the crustacea and the rotifers. Their dry organic matter constitutes about six per cent of the total organic matter of the plankton (Birge and Juday, p. 155). There would seem therefore to be so much organic matter in a particulate form as to constitute a sufficient food supply for the eaters; and this conclusion seems to hold true even after making all reasonable deductions for those

algae, etc., which may add to the total organic matter without adding to the available food supply.

On the other hand, the dissolved organic matter of lake water, if it is to be judged by amount and chemical composition, constitutes a potential food supply several times as large as that offered by the plankton. Whether it can be actually utilized as food under any conditions is a matter still waiting for investigation. Our ignorance is still complete both as to the general aspects and the innumerable details of this central problem in the nutrition of the fresh water plankton.

[1] "The Inland Lakes of Wisconsin; The Plankton, Its Quantity and Chemical Composition," *Wis. Geol. and Nat. Hist. Survey., Bull.*, **64**, Madison, 1922.

[2] "The Forms of Nitrogen Found in Certain Lake Waters," *J. Biol. Chem.*, **63**, Baltimore, 1925.

[3] Peterson, Fred and Domogalla. "The Occurrence of Amino Acids and Other Organic Nitrogen Compounds in Lake Water," *J. Biol. Chem.*, **73**, Baltimore, 1925.

[4] Moore, B., and others. "The Nutrition and Metabolism of Marine Animals," *Biochem. J.*, **6**, Liverpool, 1912.

THE STRATIGRAPHIC HORIZON OF THE BEDS CONTAINING LEPIDOCYCLINA CHAPERI ON HAUT CHAGRES, PANAMA

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The stratigraphic horizon of the beds containing *Lepidocyclina chaperi* at its type-locality on Haut Chagres, Panama, has been a subject of discussion for some time. Recently there has been submitted to me for examination a collection of foraminifera made by Mr. E. Russell Lloyd at San Juan de Pequañi, upper Rio Chagres, in 1919, and deposited in the U. S. National Museum. The collection is entered in the U. S. Geological Survey record book of localities as no. 8400. The material is a cream colored, rather soft, argillaceous limestone. The species represented are as follows:

Operculina sp., cf. *O. ocalana* Cushman (**1**, p. 129, pl. 19, figs. 4, 5).

The specimens resemble *O. ocalana* but are smaller and the number of chambers is about 21, a few more than in *O. ocalana* which usually has about 18 chambers.

Heterostegina ocalana var. *glabra* Cushman (**1**, p. 131, pl. 21, fig. 19).

The specimens of this species are small, but I was unable to discover any critical difference between them and *H. ocalana* var. *glabra*.

Discocyclina sp.

A single specimen of *Discocyclina* is contained in the collection. It is compressed, lenticular in form, very slightly umbonate and 5 mm. in diameter. Its surface is

very minutely papillate. Although similar to *D. flintensis* (Cushman) in form and size the granulations of its surface are much finer. The equatorial chambers have the rectangular form characteristic of *Discocyclina*.

Asteriacites georgiana (Cushman) Vaughan. *Orthophragmina georgiana* Cushman (**2**, p. 117, pl. 41, figs. 2, 3, pl. 42, fig. 3, pl. 43, figs. 2, 3; **3**, p. 45, pl. 10, fig. 1) *Asteriacites georgiana* Vaughan (**1**, p. 793).

Eight fragments of this species were picked out of the material, one of which is broken on one side parallel to arms which meet in the center and represents more than half of an entire specimen. This fragment is 6 mm. in diameter along a diagonal. The equatorial chambers are rectangular. The specimens conform in size, shape, ornamentation of the surface and structure to *A. georgiana*.

Lepidocyclina chaperi Lemoine and R. Douvillé (**1904**, p. 14, pl. 2, fig. 5); *Amphilepidina chaperi* H. Douvillé (**2**, p. 44, pl. 2, figs. 1, 2, text figs. 36, 37 a-d); *Amphilepidina chaperi* Vaughan (**1**, p. 798). **Not** *Lepidocyclina chaperi* Cushman (**4**, p. 92, pl. 35, figs. 1–3, pl. 36; **3**, p. 64, pl. 22, figs. 3, 4.)

Lepidocyclina chaperi is the most abundant species in the collection, it being represented by both macrospheric and microspheric specimens. The descriptions and figures of Lemoine and R. Douvillé and of H. Douvillé are good, but I doubt that the specimens from Salt Mountain and from southwest of Whatley, Clarke Co., Alabama, referred by H. Douvillé to *L. chaperi*, (**2**, p. 45, figs. 38 a-b, 39 a-b) are really *L. chaperi*, for the embryonic chambers of the specimens from these localities are smaller than those figured for topotypes of *L. chaperi* and other differences are suggested by the figures. The *Lepidocyclina chaperi* of Cushman from the Canal Zone is a different species.

Lemoine and R. Douvillé describe the embryonic chambers of *L. chaperi* as being subequal, of the American type. H. Douvillé considers them nephrolepidine and proposed the new subgenus *Amphilepidina* for those species of *Lepidocyclina* which have nephrolepidine embryonic and spatulate equatorial chambers, and refers *L. chaperi* to it. I do not see the necessity for such a subgenus.

I made a number of preparations to show the embryonic chambers of the specimens I have studied. The chambers are subequal, but one is somewhat larger than the other and the separating wall is curved. H. Douvillé's fig. 37d (*op. sup. cit.*) represents the usual condition.

In one of my papers (Vaughan, **1**, p. 798) I said that *L. undosa* Cushman from the Antiguan Oligocene is probably a synonym of *L. chaperi*, but I now know that they are distinct. The granulations of the surface of *L. undosa* are not so coarse and its embryonic chambers are of extreme nephrolepidine character grading over to the eulepidine type.

I have not yet recognized *L. chaperi* in any collection I have examined except the one from the type locality.

Lepidocyclina sp. indet.

This species is represented by a single specimen. The test is inflated in the central portion and is margined by a thin edge. Diameter, 4 mm.; thickness through the center, 2 mm.; thin margin about 0.75 mm. wide. Over the center there are on one side of the test 13 large knob-like papillae, the largest 0.5 mm. in diameter, separated by interspaces about 0.25 mm. across; on the other side there are 10 large knobs and about two smaller ones at the periphery of the larger. Around the periphery of each knob there are short thin radiating plates, about 10 were counted around one knob. The outer ends of the plates are connected by a thin calcareous ring. Outside the rings the tissues appear to be vesicular. The lateral chambers were cut away from a small area near the margin to expose the equatorial chambers, which are of lepidocycline character, rhomboid appears to be the usual form. The embryonic chambers are unknown.

Such features as can be distinguished from an examination of the exterior of the specimen agree with the description of *Lepidocyclina morgani* by Lemoine and R. Douvillé (**1904,** p. 17, pl. 2, figs. 4, 12) except that *L. morgani* is regularly discoid, never developing a projecting thin margin ("collerette") with increasing age. The profiles of *L. morgani* are distinctly different from the species here described, which has a well developed, relatively wide thin margin. The equatorial chambers near the periphery appear to be similar to those of *L. morgani* (*op. cit.*, pl. 3, fig. 2.)

Because only one specimen is available for study and consequent inability to ascertain the features of the embryonic chambers no name is attached to this obviously new species.

Lemoine and R. Douvillé in their original description of *Lepidocyclina chaperi* did not refer the species to any horizon, merely giving the locality as "Isthme de Panama (Haut-Chagres, San Juan)."

H. Douvillé (**1**, p. 130) says regarding a specimen from "Haut Chagres," that it contains small Nummulites, large Lepidocyclines near *L. chaperi*, and small stellate *Orthophragmina* (*Asterodiscus*). He referred the deposit to a lower Stampian horizon.

In 1919 (Vaughan, **2**, p. 549, table opposite p. 595) I followed H. Douvillé, an opinion in which Cushman did not concur (Vaughan, **2**, footnote to table *sup. cit.*).

H. Douvillé (**1**, p. 45) has continued to refer *L. chaperi* to an Oligocene horizon.

In 1924 (Vaughan, **3**, table 3, opposite p. 720) I referred the beds with *Orthophragmina* on Haut Chagres to the upper Eocene and (Vaughan, **1**, p. 798) queried the Oligocene age of *Lepidocyclina* (*Amphilepidina*) *chaperi*.

The list of species at San Juan Pequañi with their distribution elsewhere is as follows:

Names of species	Distribution
Operculina sp. cf. *O. ocalana* Cushman	Ocala limestone of Florida and Georgia
Heterostegina ocalana var. *glabra* Cushman	Ocala limestone of Florida
Discocyclina sp.	Known only from the Eocene in America
Asteriacites georgiana (Cushman) Vaughan	Eocene Ocala limestone of Georgia and Florida
Lepidocyclina (*Nephrolepidina*) *chaperi* Lem. and R. Douv.	Known only from the type locality.
Lepidocyclina sp. indet.	Known only from San Juan Pequañi

Conclusions.—The stratigraphic horizon of the beds in which *Lepidocyclina chaperi* occurs at San Juan Pequañi, Haut Chagres, Panama, is upper Eocene, virtually the same as that of the Ocala limestone of Florida and Georgia. *Lepidocyclina chaperi* is, therefore, an Eocene species. The only other large species of *Lepidocyclina* with nephrolepidine embryonic chambers known from America is *L. fragilis* Cushman, but the two species are so different that detailed comparison is not necessary. *L. chaperi* is different from the species from the lower Miocene Culebra formation

of the Canal Zone erroneously referred to *L. chaperi* by Cushman, and it is different from *L. undosa* Cushman from the Antiguan Oligocene, a species which I had supposed might be synonymous with it. *L. chaperi* is as yet certainly known only from its upper Eocene type locality.

Cushman, J. A. 1. American species of *Operculina* and *Heterostegina* and their faunal relations: *U. S. Geol. Survey Prof. Paper*, **128**, pp. 125–137, pl. 3, 18–21; 1921.

2. Orbitoid foraminifera of the genus *Orthophragmina* from Georgia and Florida: *U. S. Geol. Survey Prof. Paper*, **108**, pp. 115–124, pls. 40–44, 1917.

3. American species of *Orthophragmina* and *Lepidocyclina: U. S. Geol. Survey Prof. Paper*, **125**, pp. 39–105, pls. 7–35, 1920.

4. The larger fossil foraminifera of the Panama Canal Zone: *U. S. Nat. Mus. Bull.*, **103**, pp. 89–102, pls. 34–45, 1918.

Douvillé, H. 1. Les couches à Orbitoides de l' isthme de Panama: *Soc. géol. France Compte rendu somm.*, Déc. 20, 1915, pp. 129–131, 1915.

2. Revision des Lépidocyclines: *Soc. géol. France* (n. s.), *mém.*, no. **2**, pp. 49, 2 pls., 47 figs. in text, 1924.

Lemoine, R., and Douvillé, R. Sus le genre *Lepidocyclina* Gümbel: *Soc. géol. France mém.*, no. **32**, pp. 41, 3 pls., 4 figs. in text, 1904.

Vaughan, T. W. 1. American and European Tertiary larger foraminifera: *Geol. Soc. Amer. Bull.*, **35**, pp. 785, 822, pls. 30–36, 6 figs. in text, 1924.

2. The biologic character and geologic correlation of the sedimentary formations of Panama: *U. S. Nat. Mus. Bull.*, **103**, pp. 547–612, 1919.

3. Criteria and status of correlation and classification of Tertiary deposits: *Geol. Soc. Amer. Bull.*, **35**, pp. 677–742, 1924.

THE ELECTRICAL CONDUCTIVITY OF LIQUID CYANOGEN BROMIDE

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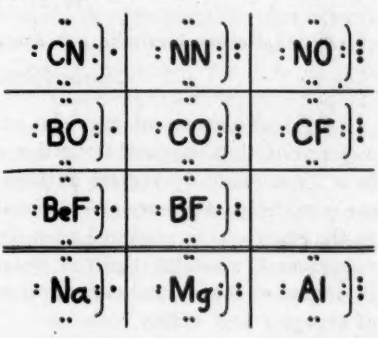
In this note I wish to record the fact that liquid cyanogen bromide at a temperature of 55°C. conducts electricity. The specific conductance of the liquid is approximately 0.02 mhos per centimeter cube.

It may be of interest to give the reasoning that led me to expect that cyanogen bromide would conduct. In a very interesting paper H. Grimm[1] has pictured a type of molecule which he calls a "pseudo atom." Methane, for instance, is a pseudo atom of neon, since the carbon nucleus and the four protons have a total positive charge of ten as has the single neon nucleus. The outer electronic structure of methane and neon are quite similar on this theory and the interesting feature concerning a pseudo atom is the complex nuclear center.

This same idea has lately come into the foreground in the theory of band

spectra.[2] The accompanying table contains a schematic representation of the possible pseudo atoms formed by the elements lithium to fluorine. It should be noted that Langmuir as early as 1916 proposed a structure for nitrogen and carbon monoxide, which resembles the above very closely.



It is interesting to study this table from a chemical point of view. For the present purpose I wish to point out that cyanogen radical is on this theory like sodium atom and therefore its fused salts should conduct electrically.

This reasoning led me to study the electrical conductivity of cyanogen bromide. A small conductivity cell having platinum electrodes 1 square centimeter in area and 1 cm. apart showed a resistance of only 200 ohms. The cyanogen bromide used was obtained from the Research Laboratories of the Eastman Kodak Co. It was not further purified. The whole material melted at 52°C. The conductivity of the molten substance was determined at 55°. I also studied the electrolysis of molten cyanogen bromide. The following observations were made in a U-shaped cell having platinum electrodes: (1) At the negative pole a colorless gas is given off which does not attack the electrode. (2) At the positive pole at first no gas is given off, but after a while the platinum assumes a reddish color and finally some gas bubbles appear. (3) The color of molten cyanogen bromide is yellowish brown. During electrolysis this color becomes lighter in shade around the negative pole and deeper in shade around the positive pole. (4) Some crystals of solid cyanogen bromide which were located above the liquid in the positive pole compartment assume a distinctly reddish color.

These experiments are only to be regarded as preliminary. The products of the electrolysis must be analyzed. This I hope to do in the near future.

I believe that a further careful study of the conductivity of cyanogen bromide will yield interesting results regarding its structure. And furthermore that a detailed analysis from a chemical point of view of table 1 should give us an idea as to whether or not the pseudo atom will prove a fruitful concept in chemistry.

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[1] *Zs. Electrochem.*, **31**, 474 (1925).

[2] R. S. Mullikan, *Physic. Rev.*, **26**, 561 (1925); R. T. Birge, *Nature*, Feb. 13 and 27, 1926.

ON THE FREE ENERGY OF HYDRATION OF IONS

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§ 1. Calculations of the heat of hydration of gaseous ions, on the assumption that the total hydration effect is of simple electrostatic origin, have been made by several authors.[1,2,3] In such calculations, the ions are considered as spheres and the heat of hydration is assumed to be equal to the energy to be obtained from discharging the spheres in vacuum and subsequently charging them in water. The formula ordinarily obtained by means of these simple assumptions for the heat of hydration of an ion of charge e and radius r_0, is:

$$\frac{e^2}{2r_0}\left(1 - \frac{1}{\epsilon}\right)$$

where ϵ is the dielectric constant of the water at the temperature chosen for the calculation.

A consideration of the principles involved leads to the following conclusions:

(1) That the energy change represented above is a free energy change,[4] since it represents the electrical work to be obtained, at constant temperature and pressure, from charging a spherical condenser in water and subsequently discharging it in vacuum; also, that the free energy change of this process is not equal to the total energy change, since ϵ, and presumably r_0 also, have temperature coefficients;

(2) that the dielectric constant of a molecular medium is not constant in the immediate vicinity of an ion, and, in accord with plausible theoretical considerations, at distances of about 1 Å from the ion, it falls almost to the value corresponding with the optical polarizability of the medium;[5,6]

(3) that the radius effective for considerations such as the above is the radius of the cavity surrounding the ion, in which there are no solvent molecules, and, therefore, that it is not to be expected that the radius found applicable for such processes would agree with that obtained in other ways;

(4) that, even though no chemical combination takes place between ions and solvent, the electrical energy associated with the hydration of an ion is not the total free energy change of the process, since there is an energy change due to the compression of the solvent in the vicinity of the ion.

The fact that $1/\epsilon$ is small in comparison with unity does not, in any degree, justify inappropriate substitutions therefor, since the purpose of

the calculations is to show the dependence of the energy of hydration upon the dielectric properties of the solvent, as well as upon the charge and effective radius of the ion. For example, in comparing the free energy of hydration with the free energy of alcoholation in such a way as to obtain the free energy of taking an ion from water to alcohol, the first terms of each expression cancel and only the terms involving the dielectric constants of the solvents remain—the compression work for the moment being neglected. It is true, nevertheless, that the difference between the free energy of hydration and of alcoholation is small, amounting usually to about three kilogram calories per mole of ions, but it is precisely this small difference which is important in determining comparatively great differences in the solubilities of electrolytes in different solvents and in determining comparatively great differences in the absolute activities of ions in different solvents.

With the principles outlined above in mind, the author has attempted to calculate the free energies of hydration of various ions. As the complete calculations are to be published elsewhere, it is the purpose to give here only an advance, summarizing report.

§ 2. The electrical contribution to the free energy of hydration is obtained by calculating the difference between the energy residing as a result of the charge in the entire volume of water surrounding an ion and that residing, also as a result of the charge, in the equivalent volume when the ion is in vacuum. The difference is clearly the electrical contribution to the free energy of hydration, since the energy residing within the cavity (in which there are no solvent molecules) is the same whether the ion is in vacuum or in some solvent. Thus the electrical contribution to the free energy of hydration is the electrical work resulting from the effect of the ions on the solvent. When the ion is in vacuum, the energy residing in that part of the field of the ion, which is exterior to a sphere of radius r_0, is $e^2/2r_0$. The energy residing in the corresponding volume, when the ion is in water, is more difficult to evaluate because of the attraction of the water dipoles to the ion, resulting in an electrical saturation effect and thus in an effectively inconstant "dielectric constant." The evaluation of this quantity may, however, be carried out in the following manner: by calculating the energy density residing at points variantly distant from the ion, at the end of a process by which the charge on the ion has been changed in infinitesimal steps from zero to its full value, and then by integrating the energy density over the entire volume of solvent which surrounds the ion, i.e., the limits of integration are $r = \infty$ and $r = r_0$, where r_0 is the radius of the cavity surrounding the ion, in which there are no solvent molecules. This radius is several times larger than the radius of the actual electronic structure of the ion, and it is this fact which justifies the approximation that the cavity is spherical. The radius

of this cavity will be referred to hereafter in this paper as the *radius of the ion*, and will be designated by r_0.

The change in energy density at a point in a medium, resulting from the change in charge giving rise to the energy, is given by the following equation:

$$\delta w = \frac{\mathrm{E}\delta D}{4\pi}$$

in which E is the electric field strength and D is the dielectric displacement. Whence the energy density residing at a point, at the end of the charging process mentioned above, is:

$$w_e = \frac{\mathrm{E}_m^2}{8\pi} + \int_0^{P_m} \mathrm{E}(P)dP$$

where P is the electric polarization of the medium at a given point at a given moment of the charging process, and is related to D and E by the following expression:

$$D = \mathrm{E} + 4\pi P.$$

It is calculable, in accordance with considerations advanced by Langevin[7] by means of the following equation:

$$P = n\alpha K + n\mu \left[\coth\left(\frac{\mu K}{kT}\right) - \frac{1}{\frac{\mu K}{kT}} \right]$$

where α is the optical polarizability of the water, K the internal field strength,[8] n the number of water molecules per cubic centimeter, μ the permanent electric moment of the water molecule, k Boltzmann's constant, and T the temperature. P_m and E_m are the values of P and E, respectively, at the end of the charging process, at a given point. The total electrical energy residing in the medium as a result of the charge is:

$$W_e = \int_{r_0}^{\infty} (w_e)\, 4\pi r^2 dr.$$

In terms of the charge on the ion, the internal field strength, the polarization and the properties of the medium, this expression becomes:

$$W_e = e^{3/2} \int_0^{K_0} \frac{1 + 2\Lambda'}{(K_m + 2\Lambda_m)^{5/2}} \cdot \left[K_m^2 \left(\frac{1}{4} - \pi n\alpha\right) + \Lambda_m K_m - \frac{\Lambda_m^2}{2} - 2\pi nkT \log \frac{\sinh \frac{\mu K_m}{kT}}{\frac{\mu K_m}{kT}} \right] dK_m$$

where e is the charge on the ion, $\Lambda = 4\pi P/3$, $\Lambda' = \partial\Lambda/\partial K$ and K_0 is the value of the internal field strength at the surface of the cavity, i.e., the internal field strength corresponding with the radius r_0.

§ 3. The compression work per unit volume, at a point, resulting from the pressures near the ion, is:

$$W_r = \int_0^{P_m} \kappa p dp$$

where κ is the coefficient of compressibility of the solvent and is itself a function of the pressure,[9] and p_m is the pressure existing at the given point, at the end of the charging process. The pressure is calculated by means of the following formula:

$$p_m = \int_0^{E_m} P dE.$$

The total compression work is obtained by graphical integration:

$$W_c = \int_{r_0}^{\infty} (w_r)\, 4\pi r^2 dr.$$

The sum of W_e and W_c, both of which can be expressed as a function of the radius of the ion, gives the free energy of hydration of a chemically unhydrated ion as a function of its radius.

§ 4. The assignment of radii (and subsequently free energies of hydration) to actual ions, may be made after the calculation of an additional property as a function of r_0; in this way, two equations are to be obtained which give two experimentally measurable properties of an electrolyte as a function of the radii of its ions. The free energy of hydration of an electrolyte is one such property; the partial molal volume at great dilution, another. The solution of the equations thus obtained yields values for the individual radii and free energies of hydration of the ions.

The change in volume of a quantity of water by the introduction of an ion is the result of two effects: (1) the volume of the ion itself (i.e., the electronic structure) and the free space surrounding it, i.e., precisely the volume of the cavity surrounding the center of the ion, in which there are no water molecules; (2) the contraction of the water as a result of the pressures arising from the attraction of the water dipoles by the ion. The effective volume of the ion is simply:

$$\frac{4}{3}\pi r_0^3.$$

The contraction of the water per unit volume at a point distant r from the center of the ion is:

$$-\frac{\Delta V_r}{V} = \int_{r_0}^{p_m} \kappa(p) dp$$

and the total contraction is:

$$-\Delta V = \int_{r_0}^{\infty} \left(-\frac{\Delta V_r}{V}\right) 4\pi r^2 dr$$

whence the partial molal volume of an ion may be calculated as a function of the radius, at dilutions sufficiently great that the field of one ion does not affect appreciably that of another. For the ions A and B of an electrolyte AB:

$$\psi(r_A) + \psi(r_B) = W_{AB}$$

$$\frac{4}{3}\pi r_A^3 + \frac{4}{3}\pi r_B^3 - f(r_A) - f(r_B) = \Delta V_{\text{total}}$$

where $\psi(r)$ is the function of r giving the free energy of hydration of an ion and $f(r)$ is the function of r giving the contraction of the solvent. W_{AB} is obtainable from experimental measurements of electrode potentials, ionization potentials, free energies of sublimation, etc., and thus: ΔV_{total} is obtainable from density measurements of very dilute solutions of the electrolyte. Table 1 has been prepared by means of equations similar to the above.

TABLE 1

ION	RADIUS (r_0)	FREE ENERGY OF HYDRATION
Na^+	1.505 Å	99.0 k. cal. per mole
K^+	1.873	81.9
Rb^+	2.02	76.9
Cs^+	2.19	71.5
F^-	1.75	87.0
Cl^-	2.238	70.1
Br^-	2.38	66.2
I^-	2.60	61.0
H^+	<0.5	249.6
Ag^+	1.57	95.5
Tl^+	1.96	78.6
Zn^{++}	1.04	525
Cd^{++}	1.15	473
Hg^{++}	1.11	486
S^{--}	4.12	54

Instead of applying the equations directly to any one electrolyte, the simplest ones of which would have necessitated the use of very uncertain values for the electron affinities of the halogens, resort has been made to the alternative of applying the equations to the difference of the two quantities for sodium and potassium ions. The value of these two radii having been obtained, the values of others may be readily calculated from the densities of the dilute solutions of their compounds. This method was used for the halogens in particular, since accurate values for the electron affinities are not to be obtained. In the case of ions for which the ionizing potentials are known, as well as standard electrode potentials and free energies of sublimation, the free energies of hydration were calculated with

reference to sodium, potassium or other ion for which he values had been obtained. The above procedure implies the assignment of absolute, single potentials, but only for a sort of ideal electrode, i.e., one for which the electrons exist as a gas in equilibrium with the solution and for which contact potentials are absent. It may be pointed out, however, that with an accurate value for the free energy of evaporation of electrons from platinum, the single potentials of gaseous electrodes employing platinum as a conductor, may be calculated.

The radii of ions here calculated (except S^{--}) follow the same order as the newer values given by Bragg[10] and by Wasastjerna[11] for the radii of ions in crystals, and indeed the differences between those here calculated and those of Bragg are roughly constant, Bragg's being about 0.47 Å smaller. When plotted against the atomic numbers, the radii of the alkali metals family and of the halogen family fall on smooth curves.

The electron affinities of the halogens calculated from the above values for the free energies of hydration, electrode potentials and free energies of dissociation are:

$$\begin{aligned} Cl &= Cl^- : 89.2 \\ Br &= Br^- : 72 \\ I &= I^- : 62 \\ {}^1/_2F_2 &= F^- : 50. \end{aligned}$$

Calculations of the above type are being extended to other than aqueous types of solutions in an attempt to calculate absolute activities of ions and relative solubilities in different solvents—even though knowledge regarding the molecular complexity of solvents is extremely uncertain.

The author takes pleasure in acknowledging his thanks to Professor P. Debye of this institute, whose advice in connection with this problem has been constantly sought and generously given.

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AN EFFECT OF TEMPERATURE AND AGE ON CROSSING-OVER IN THE FIRST CHROMOSOME OF DROSOPHILA MELANOGASTER[1]

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It has been shown by the work of Bridges[2] (1915) and Plough[3] (1917, 1921), that the percentages of crossing-over in the autosomes of *Drosophila melanogaster* are modifiable by non-genetic conditions such as physiological age and temperature. Later Mavor[4] (1923), Mavor and Svenson[5] (1924), and Muller[6] (1925), gave accounts of experiments in which females were subjected to X-rays, by which treatment the percentage of crossing-over in the X-chromosome and in the autosomes was changed. The results of these investigators all agreed that the influence of the external factors was not a general one, for not all the percentages of any given linkage test changed in a corresponding manner. There has been proven to exist a definite differential susceptibility both between different chromosomes and between regions of the same chromosome. The work of Bridges and Plough showed that there is an effect of age and temperature on the two long, V-shaped second and third chromosomes, but no effect was detected for the rod-shaped X-chromosome. Furthermore they showed that the change in recombination percentages in the autosomes is more pronounced in the central and subcentral regions of these structures. The results of the work with X-rays pointed in the same direction. Muller showed that there is a strong effect of X-raying in the middle region of the autosomes, a less pronounced effect in the adjacent regions, and no detectable effect at all in the more distant regions. Mavor published data on the influence of X-rays on the first chromosome and obtained positive results, but his findings stand alone at present in several respects (cf. also the remarks of Muller[7]).

As suggested by Bridges, the middle region of the autosomes is especially distinguished by one feature from the other parts of the chromosomes, namely that the spindle fibre is attached there. The effect of conditions modifying crossing-over might therefore be different in relation to the attachment point of the spindle fibre.

If this relation between effect on crossing-over and localization of spindle fibre attachment is not a mere coincidence but a causal connection of some kind, one would expect to find an effect of external conditions on crossing-over also in the spindle fibre region of the first chromosome.

Bridges and Plough had not found any significant change in recombina-

tion percentages in their study of the first chromosome. Plough's experiments would have enabled him to find such a difference anywhere between the locus of scute which is at 0.0 + and forked which is at 56.8. After his work was completed, Sturtevant localized a new sex-linked factor, bobbed (bb), at the extreme right end of the X-chromosome, thus extending the map to 70 units. Furthermore, Anderson,[8] Bridges and Anderson,[9] L. V. Morgan[10] and Sturtevant (unpublished) showed genetically that the *right* end of the map of the X-chromosome corresponds to the point of attachment of the spindle fibre. This region now became the most interesting one in relation to experimental changes of crossing-over, which was not taken into account by the work of Plough.

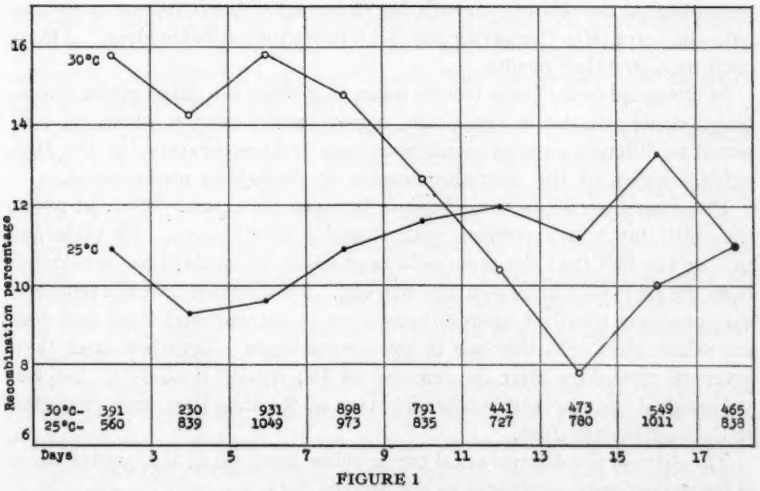

FIGURE 1

Recombination values for the loci Bar-bobbed at 25°C. and 30°C. The numbers above a given abscissa represent the numbers of flies corresponding to the temperatures indicated.

I have recently studied the problem of susceptibility of the first chromosome to external conditions modifying crossing-over by means of extensive experiments with low and high temperatures and with females of different ages in the region from garnet (44.8) to bobbed (70) which is nearest to the spindle fibre attachment. Only results obtained in the Bar-bobbed region are reported here.

Females of the constitution $\frac{B+}{+bb}$ were crossed to *bb* males. Some of the females were kept at a temperature of 25°C. as a control. Others were raised at 30°C. until hatching and were then transferred to 25°C. The newly hatched females, both control and experimental, were all kept for

three days in the first set of vials and then transferred into new vials every second day. The recombination values were determined for each period.

The results are reproduced in figure 1. The curves show two main points:

1. The females which were raised at 30°C. gave a markedly higher recombination percentage during the first three to four periods of transfers than did the control flies. The difference between the curves for recombination at 25°C. and 30°C. for the first 9 days is statistically significant (8.5 times the probable error).

2. Both curves, experiment and control, show a first minimum value at the fourth or fifth day of the age of the female. The difference in the percentage at the third to seventh day of the age of the female as compared with the seventh to thirteenth day is 3.3 times the probable error. This is confirmed by other results.

In biological terms these results mean that there is a difference in recombination percentages in genetically corresponding females which are subjected to different external conditions (age and temperature) in the Bar-bobbed region of the first chromosome of *Drosophila melanogaster*.

The disappearance of the difference between 25°C. and 30°C. at about the ninth day is in agreement with Plough's observations. He explained this by the fact that the germ cells need about seven days for developing from the early oocyte stage to the ripe egg. He assumed that the temperature produces its effect upon crossing-over at the oogonial stage and does not effect germ cells that are in the oocyte stage. Eggs laid later than seven to eight days after the removal of the female from 30°C. had not yet reached the susceptible oogonial stage at the time they were subjected to the high temperature.

The drop in the experimental curve below the level of the control curve is not statistically significant in the present data.

The results indicate that susceptibility of the process of crossing-over to external conditions is causally connected in some way with the localization of the spindle fibre attachment.

[1] The experiments have been carried out during the summer of 1925 at the Marine Biological Laboratory, Woods Hole, Mass., under a Fellowship from the International Education Board, New York.

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FORAMINIFERA FROM THE UPPER EOCENE DEPOSITS OF THE COAST OF ECUADOR

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The only previously published note, of which I am aware, on the upper Eocene of the coast of Ecuador is one by myself (Vaughan, 1, p. 869) which reads as follows:

"Specimens from the sea coast at Ancón, Santa Elena Peninsula, Ecuador, collected by H. S. Gale and F. L. Wilde, were examined by W. P. Woodring, who reports *Orthophragmina* sp., probably *O. peruviana* Cushman, *Orthophragmina* (stellate species), and *Lepidocyclina* sp., cf. *L. peruviana* Cushman. These species indicated the presence of deposits of upper Eocene age at this locality."

The collection above mentioned belongs to the U. S. National Museum and bears the U. S. Geological Survey locality number 8400.

Recently I have received additional material from the sea cliffs near Ancón, province of Guayas, Ecuador, collected by Mr. M. N. Bramlette, who has been engaged in geological field work for an oil company in that region. The two collections obviously came from the same locality or from localities very near each other. The Peninsula of Santa Elena is on the north side of the entrance to the Gulf of Guayaquil, and Ancón is about 60 miles west of the City of Guayaquil.

The material received from Mr. Gale, but collected by Mr. Wilde, is a loosely cemented gritty sandstone, most of which disintegrates when alternately wet and dried. It is composed of very angular quartz grains, feldspars in large part kaolinized, some muscovite flakes and oxidized dark minerals, among which biotite is abundant, and there are some pyroxenes. Foraminifera are abundant but most of the specimens are poorly preserved. I have extracted from the matrix *Operculina* sp., perhaps a small *Nummulites*, *Asteriacites* sp., probably *A. georgiana* (Cushman), and *Helicolepidina spiralis* Tobler. The same species can be recognized in the thin sections examined by Doctor Woodring. I found no specimens that are certainly *Discocyclina* or *Lepidocyclina*, but both genera may be present. The species are similar to those collected by Mr. Bramlette.

The specimens received from Mr. Bramlette are free from the matrix, very well preserved and suitable for detailed study. The following are notes on the species represented:

Operculina ocalana Cushman. (For references, see Vaughan, page 519.)

The general features are similar to those of *O. ocalana*, but the number of chambers in specimens 3 mm. in diameter are about 20, somewhat more than in typical *L. ocalana*, in which the usual number is about 18.

Asteriacites sp., cf. *A. georgiana* (Cushman) Vaughan. (For references, see Vaughan, page 519.)

There are five fragments of a 4-rayed species of *Asteriacites*, positive identification of which is impracticable, but it is near *A. georgiana*. The granulations over the center and along the tops of the arms are relatively coarse, therein resembling *A. georgiana* but differing from *Asteriacites asteriscus* (Guppy) from Trinidad.

The embryonic chambers are perfectly shown in one specimen which was ground on one side to the plane of the equatorial chambers. They are nephrolepidine; the smaller chamber is spherical, 0.08 mm. in diameter; the larger chamber extends from pole to pole of the smaller; the greater diameter of the entire embryonic apparatus is 0.16 mm. The equatorial chambers are very small and rectangular.

Helicolepidina spiralis Tobler (1922), H. Douvillé (1923), Vaughan (**2**, p. 802).

There are in the collection made by Mr. Bramlette 28 specimens of *Helicolepidina*, some of which do not differ significantly from a topotype of *H. spiralis* from Venezuela, received from Doctor Tobler. Others are similar to *H. spiralis* except that they are proportionately somewhat thicker through the center and have somewhat larger papillae on the central part of the test. Comparisons were also made with specimens of *H. spiralis* collected by Dr. H. G. Kugler at Soldado Rock, Trinidad. The amount of inflation of the central part of the test and the degree of development of the papillae are variable. It, therefore, appears preferable to regard the specimens differing from typical *H. spiralis* in the way above indicated as only variants of that species.

Helicolepidina appears to me to be a valid genus, an opinion different from the one I expressed in a previous paper (Vaughan, **2**, p. 802). Both it and *Spiroclypeus* are spiral in growth and both have equatorial and lateral chambers, but their equatorial chambers are very different. The equatorial chambers of *Helicolepidina* are sub-hexagonal, rhomboid, or rounded on one side, therein resembling *Lepidocyclina;* while the equatorial chambers of *Spiroclypeus* are rectangular, therein resembling *Discocyclina*, but the chambers of *Spiroclypeus* are much larger than those of *Discocyclina*. *Spiroclypeus* may be regarded as a *Heterostegina* to which lateral chambers have been added.

The upper Eocene foraminiferal fauna of Ancón, Santa Elena Peninsula, Ecuador, is different from that of the Eocene Lobitos formation of the vicinity of Paita, Peru (Bosworth, 1922, Henry Woods, 1922, Cushman, 1922, Lisson, 1922). Professor Lisson has kindly sent me topotypes of his *Lepidocyclina* (*Lepidocyclina*) *r. douvillei* from los Organos Chicos, a locality of the Lobitos formation. The species is not represented in the collection from Santa Elena Peninsula. On the other hand I have found no *Asteriacites* in the material from the Lobitos formation examined by me. The Lobitos is correlated by Henry Woods, I believe correctly, with a part of the Claiborne group of the Gulf States, and it, therefore, represents a lower horizon than the upper Eocene exposure at Ancón.

Conclusions.—The small foraminiferal fauna considered in this paper is of interest because it shows that on the Pacific coast of northern South America there are at least three Eocene horizons, the highest of which is the virtual equivalent of the Ocala limestone of the Gulf States. The horizon is also about the same as that of the exposure at San Juan Pequañi, Haut Chagres, Panama, discussed in the article on page 519.

Another interesting indication of the fauna is that it shows that during

late Eocene time the same fauna existed on both the Atlantic and Pacific sides of America and it thereby adds information on connections between the two ocean basins during Eocene time. Although the two basins probably were not continuously connected throughout the Eocene, there is evidence that they were connected during older, middle and late Eocene time.

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